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<b>(54) Title:</b> PESTICIDE COMPOUNDS, COMPOSITIONS AND PROCESS FOR THE PREPARATION THEREOF  <b>(57) Abstract</b> <p>The invention relates to compounds of general formula (I), their optically active isomers and salts wherein Ar = alicyclic, aromatic or one or more heteroatom containing heterocyclic moiety, optionally substituted by one or more alkoxy-, methylenedioxy-, alkyl-, halogen-, haloalkyl-, or nitro-group and/or condensed with a benzene ring; R<sup>1</sup>, R<sup>2</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, R<sup>3</sup>, R<sup>4</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, or R<sup>3</sup>, R<sup>4</sup> are together -O-, Y = C; PO, or YR<sup>3</sup>R<sup>4</sup> together (a) group; X = -O-, -NR<sup>10</sup>-, R<sup>9</sup> = H, alkyl, phenyl, substituted phenyl; R<sup>10</sup> = H, alkyl; R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> are independently H, alkyl, alkenyl, haloalkyl, or Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(YR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X- form together a carboximide group; E = H, halogen, methyl; m = 0, 1, 2; n = 0, 1; o = 0, 1, 2; p = 0, 1, 2, with the proviso, that the sum of the atoms or groups of the -(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X-(CR<sup>5</sup>R<sup>6</sup>)<sub>o</sub>-(CR<sup>7</sup>R<sup>8</sup>)<sub>p</sub> bridge skeleton is 3 and the -C≡C-E skeleton forms with the atoms of the bridge a linear chain, consisting of 6 atoms ending preferably in a methyl group, furthermore with the proviso, that if Ar stands for a naphthyl group, Y means C-atom, X means O-atom, R<sup>3</sup> and R<sup>4</sup> together cannot mean =O. The compounds of general formula (I) according to the invention can be applied as active ingredients of pesticide, preferably arthropodicide compositions, and as synergists of other arthropodicide active ingredients.</p> <div style="text-align: right;"><math display="block">\begin{array}{c} R^9 \\   \\ -C=N- \text{ group} \end{array} \quad (I)</math></div>		

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## PESTICIDE COMPOUNDS, COMPOSITIONS AND PROCESS FOR THE PREPARATION THEREOF

This invention relates to alkynyl pesticide compounds of the general formula I.,  
pesticide compositions containing the active ingredients of general formula I.,

- 5 furthermore the pesticide synergists of general formula I., and synergized  
pesticide compositions with known pesticide active ingredients, and the process  
for the preparation thereof.

In general formula I the substituents have the following meanings:

- 10 Ar = an alicyclic-, aromatic-, or one or more heteroatom containing heterocyclic  
moiety, optionally substituted by one or more alkoxy, methylenedioxy, alkyl,  
halogen, haloalkyl or nitro group, and/or condensed with a benzene ring,

$R^1, R^2$  = independently hydrogen, alkyl, alkenyl, haloalkyl, phenyl, substituted  
phenyl, cycloalkyl,

- 15  $R^3, R^4$  = independently hydrogen, alkyl, alkenyl, haloalkyl, phenyl, substituted  
phenyl, cycloalkyl, or

$R^3, R^4$  are together =O;

$Y = C, =PO,$  or

- 20  $YR^3R^4$  form together a  $\begin{array}{c} R^9 \\ | \\ -C=N- \end{array}$  group;

$X = -O-, -NR^{10}-;$

$R^9$  = hydrogen, alkyl, phenyl, substituted phenyl;

$R^{10}$  = hydrogen, alkyl;

$R^5, R^6, R^7, R^8$  are independently hydrogen, alkyl, alkenyl, haloalkyl, or

- 25 Ar-( $CR^1R^2$ )<sub>m</sub>-( $YR^3R^4$ )<sub>n</sub>-X- form together a carboximide group;

E = hydrogen, halogen, methyl;

m = 0, 1, 2;

n = 0, 1;

o = 0, 1, 2;

- 30 p = 0, 1, 2.

with the proviso that the sum of the atoms or groups of the bridge  $-(CR^1R^2)_m-(CR^3R^4)_n-X-(CR^5R^6)_o-(CR^7R^8)_p$  is 3 and the  $-C=C-E$  skeleton with the  
5 atoms of the bridge forms a linear chain, consisting of 6 atoms ending favorably in a methyl group.

furthermore with the proviso that if Ar is naphthyl group, Y means C-atom. X means O-atom.  $R^3$  and  $R^4$  together can not mean  $=O$ .

The invention includes furthermore the salts and the optically active isomers of  
10 the compounds of general formula I.

Narrower groups within compounds of general formula I. are represented by the compounds of general formula IA, IB, IC, ID, IE, IF, their salts and optically active isomers, where the meanings of the substituents are the same, as defined above.

15

Favourable representatives of the compounds of general formula I. are:

1-naphthyl-methyl 2-butynyl ether,

2-propynyl-1,3-benzodioxol-5-carboxylate,

1-[(2-butynyloxy)-ethyl]-3,4-dimethoxybenzene.

20 2,6-dichloro-1-(2-butynyloxymethyl)benzene.

1-[1-(2-butynyloxy)propyl]naphthalene.

R-(+)-2-[1-(2-butynyloxy)ethyl]naphthalene.

5-[(but-2-ynyloxy)methyl]-1,3-benzodioxole.

5-[2-methyl-1-(2-butynyloxy)propyl]-1,3-benzodioxole.

25 5-[(but-2-ynyloxy)phenylmethyl]-1,3-benzodioxole.

2-[(2-butynyloxy)methyl]-1,4-benzodioxane.

2,3-dihydro-2,2-dimethyl-7-(3-pentyloxy)benzofuran

In the term Ar the aromatic group is favourably phenyl or naphthyl group.

30 Ar as a heterocyclic moiety may contain one or more O, S, N heteroatoms, it may favourably represent benzodioxole-, benzodioxane-, 2-benzofuran-, 7-benzofuran-moieties.

The alicyclic group may favourably be condensed with a benzene ring, thus for instance may represent indane group, or 1,2,3,4-tetrahydronaphthyl group. The carboximide group may favourably represent phthalimide moiety.

The aromatic, heterocyclic and alicyclic Ar groups are optionally substituted by C<sub>1-4</sub> alkoxy-, methylenedioxy-, C<sub>1-4</sub> alkyl-, halogen-, C<sub>1-4</sub> haloalkyl- or nitro group.

Compounds which are non-toxic, or only slightly toxic alone, but given together with a pesticide, preferably arthropodicide agent they enhance markedly the potency of the latter, are called *synergists*. These materials may in principle act in several ways, however they exert their effect decisively by blocking the metabolism of the active substance. Metabolism may proceed via oxidative, hydrolytic, conjugative and absorption reactions and by the variations thereof. At present there is no unambiguous example for a synergist acting at the receptor level, neither do they play an important role in the praxis.

The synergistic potency e.g. in the case of insecticides is characterized by the so-called SR synergist ratio which is given as follows:

$$SR_{50} = \frac{LD_{50} \text{insecticide}}{LD_{50} \text{insecticide} + \text{synergist}}$$

The more the SR<sub>50</sub> value differs from 1, the higher is the synergistic potency. The use of synergists in arthropodicidal preparations is very attractive, since they afford a possibility to come out with new preparations with practically all representatives of the area. These new preparations, compared to the previous ones, promise to be less expensive, less toxic, more selective, encountering less environmental hazard, suppressing the evolution of resistance, and being active also on strains which already evolved resistance.

Following the discovery of synergists and the reveal of their mode of action, a wide-range research and development work started from the mid 60-ies till the late 70-ies to work out new synergists. This research, however resulted only a

few molecules which really attained application (at present the number of the registered insecticide synergists is less than 10). These compounds are of basic scientific importance in the research of resistance (K. F. Raffa and T. M. Priester, *J. Agric. Entomol.*, 2(1), 27-45, (1985)), however, there are only 2-3  
5 molecules listed as products in the Pesticide Manual, and only two materials (PBO, MGK264) which are actually on the market. The field application has been restricted by several factors: it is not easy to find a chemical tool which can be used selectively and safely, and the cost/effectiveness ratio of which is competitive with that of the active ingredient. To apply a synergist  
10 economically, it must be highly potent, it must act at small doses (not exceeding the original dose of the active ingredient).

On the basis of their chemical structures the presently known arthropodicide synergistic compounds may be divided into the following groups:

### 1.3-methylenedioxyphenyl (MDP) derivatives

15 ### O-2-propynyl and propynyl-homologues and their derivatives (ethers, oxim-ethers, esters)

### N-alkyl derivatives

### phosphor esters

### other derivatives e.g. thiocyanates, polyhalo ethers etc.

20 The compounds may also be divided into groups on the basis of their target of attack [K. F. Raffa and T. M. Priester, *J. Agric. Entomol.*, 2(1), 27-45, (1985)], but this grouping is rather theoretical, less exact, first of all because the actual metabolic processes are not fully known. The metabolism of most of the compounds proceeds consecutively, but may also proceed simultaneously, and  
25 may follow several mechanisms, thus the division is less informative, even if we consider the first step of the cascade degradation as the decisive step.

For the metabolic degradation of most arthropodicides first of all the oxygenase system is responsible. It is agreed in the literature that the compounds of this  
30 group exert their activity basically by blocking the cytochrome P-450 enzyme of the microsomal oxidation system [John E. Cassida, *J. Agr. Food Chem.*, 18(5),

- 753-772, (1970), R. M. Sacher, R. L. Metcalf and T. R. Fukuto: *J. Agr. Food Chem.*, **16**(5), 779-786, (1968)]. The enzymes forming the structurally analogous group of so-called isoenzymes constitute the major part of the detoxification system of the organisms [Ortiz de Montellano, P. R., Ed.
- 5 *Cytochrome P-450: Structure Mech. and Biochem.*, Plenum New York, (1986)]. They perform detoxification via mono-oxygenation of the substrate, producing a more polar product, which possibly after further transformations can be eliminated by the organism. The system degrades very different structures by the same way. Therefore they are also designated as Mixed Function Oxygenases
- 10 (MFO) and Polysubstrate Monooxygenases (PSMO).

On that basis one could expect that the surface of the enzyme is aspecific for the synergist, too. Quite the contrary, we have found that the compounds may be optimized.

- 15 For the isolation and testing of the Cytochrome P-450 enzymes of insects there are standard methods available [J. G. Scott and S. S. T. Lee: *Arch. Insect Biochem. and Phys.*, **24**, 1-19, (1993)]. The enzymes of various species may show great similarities, but they may also differ significantly from each other.
- The synergists known from the literature and investigated by us belong to the
- 20 group of O-2-propynyl, and propynyl-homologues and their derivatives (ethers, oxim-ethers, esters). As shown by the literature they exhibit different potency for the different species, which means that the oxidation capacity of the species varies to a certain extent. This is the reason for the high insect/mammal selectivity and synergist selectivity, characteristic for that group of compounds.
- 25 These selectivities, which cannot be directly explained by the above mode of action, are the bases of the development and safe application. On the other hand this is the reason why these compounds have not become commercially available. For all the compounds of the group prepared and evaluated so far we can tell, in general, that their effect was exclusively bound to the propynyl side-chain, this chain has been substituted in the allylic position by various aryl rings

mainly through an oxygen atom. The compounds known as yet may be divided into the following groups:

- ### Phenyl propargyl ethers [Fellig et. al., *J. Agr. Food Chem.*, **18**(5), 78, (1970)]
- 5 ### Benzyl propargyl ethers [Ciba Geigy, *Ger. Offen.* **2 235 005** (1972)]
- ### Benzaldoxime propargyl ethers [Ciba Geigy, *Ger. Offen.* **2 016 190** (1970)]
- ### Naphthoic acid propargyl esters [Hoffman-La Roche, *Belg. Patent.* **867 849** (1978)]
- 10 ### Alkynylphthalimides [FMC, *Ger. Patent.* **1 217 693** (1966)]
- ### Phenylphosphonic acid propargyl esters [Niagara Chem. Div., FMC Corp., Technical Data Sheet on NIA 16824, (1968)]

The first two groups are sub-divided into further groups owing to the high variability of the aromatic group and its substituents. Thus, there are known

15 naphthyl propargyl ethers [Hoffman-La Roche, *US* **3 362 871** (1968); Ciba Geigy, *Ger. Offen.* **2 100 325** (1971)],

4-hydroxyquinoline propargyl ethers [Alkaloida, *HU* **210 557**, (1992)],

methylenedioxybenzyl propargyl ethers [Sumitomo, *JP.* **03 01177**, (1973)] and

alfa-substituted methylenedioxybenzyl propargyl ethers [Sumitomo, *JP.*

20 **61 24585, 61 24586** (1986)].

In a study about naphthyl propynyl ethers it has been concluded that butynyl ethers, first of all 3-butynyl ethers are more potent than the analogous propargyl and pentynyl ethers [R. M. Sacher et. al., *J. Agr. Food Chem.*, **16**, 779-786, (1968)]. Interestingly, however there was no continuation of that work, the

25 discovery has not been patented, either. Detailed analysis of the literature data suggest, that the propynyl side-chain cannot be replaced by homologous chains, since the publications and patents relate further on to propargyl derivatives.

In order to clear this contraversion we have prepared the compounds in question, and found that in contrast to what was disclosed in the literature, the 2-

30 butynyl derivative (the one ending in a methyl group) is more potent than the 3-butynyl derivative; the alpha-isomers are more potent than the analogous beta-



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isomers; and the 3-pentynyl derivative is more potent than the 2-butyryl derivative. These data suit well in our theory, and the data given in the literature might be the reason why this direction was not followed by others.

Similarly, there is a contraversion regarding the activity of the 4-

- 5 pentynylphthalimide derivatives: although they proved to be potent synergists of allethrin, they antagonized with pyrethrin [H. Jaffe, J. L. Neumeyer, *J. Med. Chem.*, **13**, 901, (1970)]. In these structures again, the alkynyl chain ends in triple bond. The hybriide variations of these structures, namely the N-alkyloxy-O-propargyl-phthalimides have also been prepared, here again the triple bond is
- 10 in terminal position [Sumitomo, *NL*, **6 600 916** (1966)].

- To sum up, the most active representatives of the group, although on some tests exhibited outstanding activity, and were superior regarding their synergist/active ingredient ratio [D. J. Henessy, *Biochemical Toxicology of Insecticides*, Ed., R. D. O'Brian & I. Yamamoto, Academic Press, 105-114, (1970)], have never been
- 15 applied in the praxis. This has several reasons: their activity did not reach the potency of earlier, well-established derivatives, they exhibited activity only in a narrow range, their potency was highly species-dependent, and within one species it depended greatly on the "strength" of the individual. Their safe and broad application was not therefore ensured.

- 20 The alkynyl compounds listed above are all derivatives of a common optimal structure, but the authors did not realize the relationships, and have not prepared the most active representatives, alloying and improving the advantages of these groups of compounds.

- We have experimentally tested, compared and analysed the biological effect of
- 25 the known compounds, as well as that of the new derivatives prepared by us, and revealed the structural element which is responsible for the effect. On that basis we have prepared new compounds which surpass significantly the activity of the earlier ones and combine those properties which ensure effectiveness on more species and with more known active ingredients.

- 30 The integral part of the present invention is the discovery, that in the optimal compounds the carrier of the activity is a triple bond of an alkynyl structure with

an electron-rich Ar ring, which is connected to the triple bond through a mobile bridge consisting of three atoms. The atoms of the bridge are variable, and may have substituents, and so is the ring. To enhance the activity it is favourable to introduce lipophilic and electron-rich atoms and substituents. Thus the atoms of the bridge may be -besides of carbon atoms- oxygen, sulphur, nitrogen, and phosphor heteroatoms. These atoms may be linked through single or multiple bonds to each other and optionally with further substituents containing the above heteroatoms they may be substituted to further functional groups or derivatives. The atoms may be replaced by each other. The first element of the bridge may with its substituent form a ring, which may be attached to the aromatic ring, and thus may be part of the electron-rich moiety. Into the ring, linked to the bridge, heteroatoms, as listed above, may also be incorporated, and the effect may be further enhanced by the introduction of alkoxy, halogen, alkyl, haloalkyl or nitro substituents. The ring may be 5-, 6-, or 7-membered and may be condensed with a further ring, which is built according to the above principles, and may incorporate the first element of the bridge. Compounds in which the acetylenic hydrogen of the alkynyl side-chain is replaced by a methyl group exhibit higher activity than the the analogues with terminal triple bond. Keeping these rules we can carry out new substitutions by which we can modify the character of the compounds, according to the demand (lipophilicity, translaminarity, systemicity, etc.) of the application area.

Of the isomers of optically active compounds, e.g.  $\alpha$ -methyl-substituted benzyl derivatives, the R(+)-enantiomers are more potent than the S(-)-enantiomers. The difference between the activities of the isomers is growing with an enhancing activity of the racemic mixture.

The compounds developed by us are new, they are characterized by outstanding mammal/insect selectivity and high potency, exerted at low dose related to the active ingredient. This is attributed to the outstanding high receptor affinity of our compounds. In comparative experiments the indices of our compounds

highly surpassed those of earlier known synergists for active ingredients, whose metabolism is based on microsomal oxidation. This high activity and selectivity were also demonstrated in field studies conducted on small plots. The compounds did not show fito-toxicity, they did not separate from the active ingredients. their physico-chemical parameters fitted well with those of the active ingredient. Through these features the dose/efficacy/cost value, which earlier hindered the application, could favourably be modified and the application became possible.

With the active substances of general formula I the effect of the following known arthropodicide active ingredients may favourably be synergized:

Acetamide derivatives: e.g. oxamyl;

Benzoylurea compounds: e.g. flucycloxuron, hexaflumuron, teflubenzuron, triflumuron;

Benzoylurea like IGR compounds;

Bicycloheptadien compounds: e.g. heptenophos;

Cross-bridged diphenyl compounds: e.g. etofenprox, bromopropylate, methoxychlor, temephos, tetradifon;

Carbamates: e.g. aminocarb, aldicarb, aldoxycarb, asulam, bendiocarb, benfuracarb, carbaryl, carbetamide, carbofuran, carbosulfan, diethofencarb, dioxacarb, ethiofencarb, fenobucarb, fenoxycarb, furathiocarb, isoprocarb, methomyl, oxamyl, pirimicarb (pirimor), propoxur, thiodicarb, thiofanox, xylylcarb;

Carbamoyloxime derivatives: e.g. alanycarb, butocarboxim;

Cyclodienes: e.g. aldrin, chlordane, endosulfan, heptachlor;

Diazoles: fipronil;

Hydrazides: RH 5992, RH 5849, CGA 215'944;

Nereistoxin analogues: pl. bensultap;

Nitroimidazolidinylenamines: e.g. imidacloprid;

Organophosphor compounds e.g. quinalphos, diazinon, phosalone, dimethoate, azinphos-methyl,

Organotin compounds e.g. azocyclotin, cyhexatin, fenbutatin oxide SSI-121;

- Phenoxy compounds: e.g. diafenthiuron;  
Pyrazoles: e.g. pyrazophos;  
Pyrethroides: e.g. allethrin, bioallethrin (esbol), acrinathrin, fenvalerate, empenethrin, prallethrin, resmethrin, MTI-800, flufenprox, permethrin,  
5 tetramethrin, cypermethrin and their isomers and isomer-combinations:  
Pyridazinones: e.g. pyridaben;  
Pyridine derivatives: e.g. chlorpyrifos;  
Pyrimidine derivatives: e.g. pyrimiphos-ethyl, pyrimiphos-methyl;  
Pyrroles: e.g. AC 303-t. 630;  
10 Quinazolines: e.g. fenazaquin;  
Terpenoid derivatives: e.g. methoprene;  
Tetrazines: e.g. clofentezine, SZI-121 (flufenzin);  
Thiadiazines: e.g. buprofezin;  
Thiazolidin: pl. hexythiazox;  
15 Triazoles: pl. isazophos, RH 7988;  
Chlorinated hydrocarbons: lindane;  
Macrocyclic lactones;  
Tebufenpyrad;  
Fenpyroximate;  
20 Triazamate;  
The above known active ingredients are described in the 8th and 10th Edition of the Pesticide Manual, European Patent Application No. 0635499 (SZI-121), A.G.Chem.New Compound review vol. 11(1993) and ACS Symposium Series 504 p. 272. respectively.  
25 Compounds of the general formula I can be most preferably used to synergize the effect of carbamates preferably carbofuran.  
We have found that the compounds have dual action, they are superior synergists of arthropodicide active ingredients, and they also hinder the individual growth of arthropoda through an effect impeding the biosynthesis of  
30 ecdison, a material, playing key role in the growth of arthropoda. There is thus an unambiguous relationship between the synergistic- and the individual

growth-hindering activities. This latter effect, beside the outstanding metabolism-blocking activity of the compounds, is also a consequence of the fact, that these materials, in contrast to the other, earlier known families of compounds, practically do not degrade, or degrade only extremely slowly in the organism of the arthropoda. Thus, when applied alone, at a long run, depending on the periods of the endocrin regulation, they are able to block the hormon synthesis and hinder the degradation of the endo and exo-biotica. Due to the toxins accumulating in the organism, the individuals become incapable of living, they do not eat, the production of eggs diminishes, and the reproduction stops.

Beside these enhanced activities, the toxicity values of the compounds on mammals did not increase. This can be attributed to the differences in the electrode potential values of microsomal oxidation systems for mammals and for arthropoda. Whereas the oxidation potential values of the higher-order organisms are high, and therefore they are able to beat the electron-barrier of the complexed synergists, the oxidation system of the arthropoda, with its small potential, is not capable to oxidate, and by this to remove the complexed molecule from the surface of the enzyme, causing the paralysis of the system. This is the reason why the compounds can be applied safely and selectively. The over-average fast degradation and excretion of the compounds from mammalia, owing to their high enzyme activity and fast enzyme binding, ensure, in contrast to the arthropoda, that these materials do not enhance the effect of biotics found or taken up by the mammalian organism, and therefore they are safe.

The effect was demonstrated by us on various arthropode species. Applied alone, or as a synergist, the compounds were active on insects, plant-louses and also on acari. In the light of the above, this fact refers again to the qualitatively different detoxification system of the mammals.

A very valuable advantage of our compounds is that on applying them to species, which already evolved resistance, the toxic dose could be reduced below the original dose of the known active ingredient (measured on susceptible strains). This has not been experienced with other synergists. This makes

possible the safe and effective management of resistant populations, complying with the modern regulations.

Beside the expected advantages mentioned above (they make possible to develop tools which are less expensive, less toxic on mammals, selective, and can suppress resistance) with the help of these compounds a number of well-established active ingredients can be renewed, the market of which has fallen back in the past years, because resistance evolved against them. (Carbofuran, Quinalphos, Cartap, Methomyl). Our compounds create new application and market possibilities, since they enhance the potency of less active materials (Resmethrin, Bioallethrin, Pirimicarb etc.) to the level of the most active compounds, without increasing their toxicity. PBO, which is on the market in big lots, but -with natural resources running low- at increasing price, and which is drawing back because of its suspected tumor provoking effect, may also be replaced with the help of our compounds.

The preparation of the compounds of general formula I varies depending on the different groups of compounds, and can be carried out by the chemical methods, characteristic for the preparation of these groups.

Thus

a.) for the preparation of compounds of general formula IA, where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meaning as defined above, compounds of general formula II and III are reacted wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meaning as defined above, A and B are groups, suitable to form ester bond.

b.) for the preparation of compounds of general formula IB, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, Y, E, m, o, and p, have the same meaning as defined above.

compounds of general formula IV and V are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meaning as defined above, and C and D stand for groups, suitable to form amide bond.

- c.) for the preparation of compounds of general formula IC, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meaning as defined above, R<sup>3</sup> and R<sup>4</sup> independently mean H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl.
- 5 compounds of general formula VI and VII are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meaning as defined above, R<sup>3</sup> and R<sup>4</sup> may independently mean H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, F and G stand for groups, suitable to form ether bond,
- 10 d.) for the preparation of compounds of general formula ID, wherein Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>2</sup>R<sup>4</sup>)<sub>n</sub>-N- stands for caboximide group, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, o, and p, have the same meaning as defined above,  
the carboximide of general formula VIII is reacted with the compounds of general formula IX, wherein R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, o, and p, have the same  
15 meaning as defined above and Lg stands for a leaving group,
- e.) for the preparation of compounds of general formula IE, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, E, m, n, o, and p, have the same meaning as defined above,
- 20 compounds of general formula X and XI are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meaning as defined above.  
H and I stand for a group, suitable to form a  

$$\begin{array}{c} \text{-N-} \\ | \\ \text{R}^{10} \end{array}$$
25 group, wherein R<sup>10</sup>, has the same meaning as defined above,
- f.) for the preparation of compounds of general formula IF, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, o, and p, have the same meaning as defined above,  
compounds of general formula XII and IX are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>,  
30 R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, n, o, and p, have the same meaning as defined above,  
and Lg stands for a leaving group, and

if desired, the compound of general formula I can be transformed into its salts, or may be liberated from its salts and, if desired, the optically active isomers can be separated.

5

To prepare the compounds of general formula I advantageously:

- a.) The acyl halide of general formula II is reacted with the alkynol of general formula III, or the carboxylic acid of general formula II is reacted with the alkynyl halogenide of general formula III, in the presence of an acid binding agent, or
- 10 the carboxylic acid of general formula II is reacted with the alkynol of general formula III in the presence of an activator, preferably diethyl azodicarboxylate and triphenylphosphine or dicyclohexylcarbodiimide and an acidic catalyst,
- 15 b.) The acyl halide of general formula II is reacted with the primary or secondary alkynylamine of general formula V, or the carboxamide of general formula IV is reacted with the alkynyl halogenide of general formula V, optionally in the presence of an acid-binding agent,
- 20 c.) The alcohol of general formula VI is reacted with the alkynyl halogenide of general formula VII, or the halogenide of general formula VI is reacted with the alkynol of general formula VII in the presence of a base, or the alcohol of general formula VI and the alkynol of general formula VII are reacted in the presence of an activator, preferably diethyl azodicarboxylate and
- 25 triphenylphosphine or dicyclohexylcarbodiimide and an acidic catalyst,
- d.) The carboximide of general formula VIII is reacted in the presence of a base with the alkynyl halogenide or -mesylate, -tosylate, -trifluoroacetate of general formula IX, or

30



e.) The secondary amine of general formula X is reacted with the alkynyl halogenide of general formula XI, or the halogenide of general formula X is reacted with the secondary amine of general formula XI in the presence of a base, or

5

f.) The aldoxime or ketoxime of general formula XII is reacted in the presence of a base with the alkynyl halogenide or -mesylate, -tosylate, -trifluoroacetate of general formula IX.

10 The compounds prepared and claimed by us are new, they are not disclosed in the literature. Their structures have been elucidated after purification, purity was checked by TLC and GC methods. The molecular formula of the compounds was proven by elementary analysis, and the structures were unequivocally supported by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR measurements.

15

The materials can be formulated as independent compositions or in admixture with other known arthropodicide active ingredients, and according to the application goal known carriers and other auxiliary materials may be used. Thus, by methods known per se, emulsion concentrates, microemulsions, dusters,

20 aerosols, vaporators and smokers may be prepared. [Rhone Poulenc-Geronazzo: Surfactant and Specialities for Plant Protection, Application Manual (1994), ICI: Surfactants, Application Manual (1992)].

In the course of the application the preparation containing the compound of  
25 general formula I and the preparation containing the known active ingredient(s) can be used one after the other or by making a tank-mixture of them.

To demonstrate the scope of our invention we present the following examples, without limiting the scope to the examples.

30

Examples for preparation:

Purity of the compounds was checked by TLC and GC methods: (CP 9000, CP-SIL-5CB, 60 m x 0.53  $\mu$ m, 5 ml/min  $N_2$ , FID, 220°C). As shown by these  
5 methods all compounds had purity over 95%. Structure of the materials was supported by IR,  $^1H$  and  $^{13}C$ -NMR measurements. molecular formulae were proven by elementary analysis.

## 1. Alkynyl esters

10

## General procedure

## A.)

The appropriate alkynyl alcohole was dissolved in dry benzene, pyridine was  
15 added and the mixture was cooled to 0-5°C. To this mixture the acyl chloride was added at a rate that the inner temperature does not exceed 5°C. The reaction mixture was stirred at room temperature overnight, the precipitated pyridinium hydrochloride was filtered off. The filtrate was neutralized with hydrogen chloride solution, then washed subsequently with water and saturated sodium  
20 chloride solution, dried on  $MgSO_4$  and evaporated. The raw material was purified by chromatography.

## B.)

6 mmol of the acide were dissolved in 20 ml of dry THF and 1.0 g (6 mmol) of diethyl azodicarboxylate (DEAD) were added. The mixture was cooled on an  
25 ice-water bath, and the solution of 10 mmol of the alkynol and 1.6 g (6 mmol) of triphenylphosphine in 10 ml of THF was added. The characteristic orange colour of the DEAD gradually disappeared. The solution was stirred at room temperature overnight, then it was diluted with 50 ml of ethylacetate, washed with saturated sodium chloride solution, dried and evaporated. From the residue

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the triphenylphosphine oxide crystallized on addition of hexane-ethylacetate mixture. The filtrate was purified by column chromatography.

	Compound	Mp(C°)	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
1.1 501	2-Propynyl 1,3-benzodioxol-5-carboxylate	69-70	3270, 3010, 2922, 2853, 2124, 1726, 1625, 1606, 1501, 1445, 1373, 1279, 1263, 1157, 1103, 1076, 1039, 762.	2.51 (1H, t, J=2.4 Hz, $\equiv$ C-H), 4.88 (2H, d, J=2.4 Hz, OCH <sub>2</sub> -C $\equiv$ ), 6.03 (2H, s, OCH <sub>2</sub> O), 6.83 (1H, d, J=8.2 Hz), 7.47 (1H, d, J=1.6 Hz), 7.66 (1H, dd, J=8.2, 1.6 Hz)	52.34 (OCH <sub>2</sub> -C $\equiv$ ), 74.92 ( $\equiv$ CH), 77.81 (OCH <sub>2</sub> -C $\equiv$ ), 101.85 (OCH <sub>2</sub> O), 107.99, 109.59 (C-4, C-7), 123.29 (C-5), 125.71 (C-6), 147.74 (C-3a), 151.91 (C-7a), 165.07 (CO ester)
1.2 502	2-Butynyl 1,3-benzodioxol-5-carboxylate	63-64	3016, 2959, 2920, 2244, 1714, 1626, 1606, 1508, 1450, 1372, 1276, 1240, 1163, 1117, 1078, 1036, 970, 925, 758.	1.86 (3H, t, J=2.3 Hz, $\equiv$ C-CH <sub>3</sub> ), 4.84 (2H, q, J=2.3 Hz, OCH <sub>2</sub> -C $\equiv$ ), 6.03 (2H, s, OCH <sub>2</sub> O), 6.83 (1H, d, J=8.2 Hz), 7.47 (1H, d, J=1.6 Hz), 7.67 (1H, dd, J=8.2, 1.6 Hz).	3.65 ( $\equiv$ C-CH <sub>3</sub> ), 53.19 (OCH <sub>2</sub> -C $\equiv$ ), 73.33 (OCH <sub>2</sub> -C $\equiv$ ), 83.17 ( $\equiv$ C-CH <sub>3</sub> ), 101.81 (OCH <sub>2</sub> O), 107.95, 109.62 (C-4, C-7), 123.69 (C-5), 125.62 (C-6), 147.72 (C-3a), 151.78 (C-7a), 165.33 (CO ester)

## 2. Alkynyl-amides

## General procedure

The solution of the acyl chloride was reacted with the solution of the alkynylamine, in the presence of pyridine, at room temperature. The suspension was diluted washed consecutively with water, diluted hydrochloric acid solution and sodium hydrocarbonate solution, dried, evaporated and purified by chromatography and crystallisation.

	Compound	Mp(C°)	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
2.1 523	N-(2-butyryl) 3,4-methylene- dioxy- benzamide	143-144	3334, 3075, 2918, 1641, 1620, 1605, 1546, 1500, 1485, 1313, 1264, 1239, 1042.	1.82 (3H, t, J=2.4 Hz, CH <sub>3</sub> -C≡), 4.16 (2H, m, NH-CH <sub>2</sub> -C≡), 6.02 (2H, s, (CH <sub>2</sub> O) <sub>2</sub> ), 6.23 (NH), 6.81 (1H, dd, J=0.6, 7.8 Hz, H-4), 7.28-7.34 (2H, m, H-6, H-7)	3.54 (CH <sub>3</sub> -C≡), 30.37 (NH-CH <sub>2</sub> -C≡), 74.72 and 79.77 (C≡C), 101.73 (OCH <sub>2</sub> O), 107.72, 108.02 (C-4, C-7), 121.70 (C-6), 128.26 (C- 5), 148.01 (C-3a), 150.49 (C-7a), 166.37 (CONH)
2.2 535	N-(2-Butyryl)- 2-naphthamide	133-134	3295 (NH), 3055, 2922, 2913, 2850, 1641, 1629, 1602, 1541, 1414, 1309, 776, 756	1.08 (3H, t, J=2.1 Hz, CH <sub>3</sub> -C≡), 3.38 (1H, s, NH), 4.10 (2H, m, CH <sub>2</sub> - C≡), 7.60 (2H, m), 8.0 (3H, m), 8.49 (1H, s, H- 1), 9.03 (1H, t, J=5.3 Hz)	3.27 (CH <sub>3</sub> -C≡), 29.11 (- CH <sub>2</sub> -C≡), 76.77 and 78.07 (C≡C), 124.29 (C- 3), 126.90, 127.82 (three signals overlapping), 128.08, 129.07, 131.51 (C-4a), 132.32 (C-2), 134.37 (C-8a), 166.07 (CO)

5	2.3 541	N-(2-Propynyl)- 1-naphthamide	105-106	3229 (NH), 3046, 2963, 2927, 2118, , 1635, 1618, 1590, 1576, 1531, 1415, 1301, 1245, 1033, 788, 773, 759, 519	2.27 (3H, t, J=2.4 Hz, H- C≡), 4.24 (2H, q, J=2.4, CH <sub>2</sub> -C≡), 6.52 (1H, broad s, NH), 7.35 (1H, t, J=8.1 Hz), 7.50 (3H, m), 7.84 (2H, m), 8.26 (1H, m)	29.62 (-CH <sub>2</sub> -C≡), 71.80 (H-C≡C), 79.43 (H- C≡C), 124.59, 125.19, 125.29, 126.41, 127.14, 128.28, 130.06 (C-8a), 130.85 (C-2), 133.34 (C- 1), 133.59 (C-4a), 169.14 (CO)
10	2.4 542	N-(2-Butynyl)- 1-naphthamide	120-122	3276 (NH), 3046, 3011, 2917, 2856, 1632, 1618, 1591, 1577, 1522, 1444, 1432, 1287, 1258, 783	1.83 (3H, t, J=2.1 Hz, CH <sub>3</sub> -C≡), 4.25 (2H, q, J=2.1 Hz, CH <sub>2</sub> -C≡), 6.25 (1H, s, NH), 7.31- 7.60 (3H, m), 7.85 (2H, m), 8.32 (1H, m)	3.50 (CH <sub>3</sub> -C≡), 30.24 (- CH <sub>2</sub> -C≡), 74.47 and 79.81 (C≡C), 124.59, 125.19, 124.62, 125.09, 125.37, 126.39, 127.10, 128.26, 130.11 (C-8a), 130.75 (C-2), 133.64 and 133.75 (C-1, C-4a), 169.03 (CO)
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20						

## 3. Alkynylimides

## General procedure

To the solution of phthalimide in dry DMF 1 molar equivalent of dry potassium carbonate was added and to this suspension was added dropwise the toluene solution of 1 molar equivalent of alkynyl bromide. The suspension was stirred at 80 °C for 3 hours, then it was poured on ice-water. the crystals were collected and crystallized from 96% ethanol.

	Compound	Mp(C°)	IR $\nu(\text{cm}^{-1})$	$^1\text{H-NMR } \delta \text{ (ppm)}$	$^{13}\text{C-NMR } \delta \text{ (ppm)}$
3.1 537	N-(But-2-ynyl)- phthalimide	216-218	3090, 3040 (H-C aromatic), 2957, 2920 (CH aliphatic), 2234 (C $\equiv$ C) 1768, 1718 (CO), 1609 (C=C aromatic), 1468, 1431, 1397, 1354, 1333, 1126, 1090, 952, 775, 732, 712, 629, 560, 532.	1.76 (3H, t, J=2.3 Hz, CH <sub>3</sub> -C $\equiv$ ), 4.32 (2H, q, J=2.3 Hz, N-CH <sub>2</sub> -C $\equiv$ ), 7.86-7.91 (4H. m, aromatic)	3.12 (CH <sub>3</sub> -C $\equiv$ ), 27.16 (N-CH <sub>2</sub> -C $\equiv$ ), 73.82 (CH <sub>3</sub> -C $\equiv$ ), 79.06 (CH <sub>2</sub> - C $\equiv$ ), 123.48 (C-3, C-6), 131.64 (C-1, C-2), 134.87 (C-4, C-5), 167.01 (CO)

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4. (Aryl-alkyl)-, alkyl-alkynyl ethers

4.0 Preparation of 1-[(2-butynyloxy)-ethyl]-3,4-dimethoxybenzene (compound 599)

In a 50 ml flask fitted with thermometer, magnetic stirrer, addition funnel, and connected to an inert gas system, the suspension of 30 ml of dry THF and 1.5 g  
5 (0.063 mol) of NaH (cca.90 %) was prepared. To the suspension was added dropwise, at room temperature the solution of 4.0 g (0.021 mol) of  $\alpha$ -methyl-  
veratryl alcohol in 21 ml of dry THF. The mixture was heated under reflux conditions for 1 hour, cooled to room temperature, 4.1 g (0.0315 mol) of 1-bromo-2-butyne were added, then the heating was continued. The reaction was  
10 followed by TLC (eluent: hexane-EtOAc 4:1). The reaction is completed in about 3-4 hours.

To the cooled thick suspension 50 ml of ether was added, the mixture was filtered on Celite, the filtrate was washed with distilled water, dried on magnesium sulfate and evaporated. The residual oil was purified by column  
15 chromatography (eluent: hexane-EtOAc 4:1,  $R_f=0.37$ ).

Yield: 2.3 g (9.8 mmol), 46.9 %.

Purity of the product was checked by GC analysis: (CP 9000, CP-SIL-5CB, 60 m x 0.53  $\mu$ m, 5 ml/min  $N_2$ , FID, 250°C)  $t_R = 12.0$  min, >99%

Proof of structure:

20 Elementary analysis: ( $C_{14}H_{17}O_3$ , 233.29):

calculated: C% 72.08, H% 7.35

found: C% 69.70, H% 7.21

IR ( $CHCl_3$ )  $\nu$   $cm^{-1}$ : 2976, 2855, 2837, 1605, 1595, 1514, 1465, 1419, 1371, 1353, 1311, 1260, 1164, 1141, 1086, 1027, 864

25  $^1H$ -NMR (200 MHz,  $CDCl_3$ )  $\delta$ :

1.46 (3H, d,  $J=6.5$ Hz,  $CH-CH_3$ ), 1.85 (3H, t,  $J=2.3$ Hz,  $\equiv C-CH_3$ ),

3.83 and 4.01 (2H, ABX<sub>3</sub>  $J_{AB}=15.0$ Hz,  $J_{AX}=J_{BX}=2.3$ Hz,  $\equiv C-CH_2O$ ),

3.87 and 3.89 (summa 6H, s each  $OCH_3$ )

4.55 (2H, q,  $J=6.5$  Hz, Ar-CHO),

30 6.80-6.89 (3H, m, aromatic).

$^{13}\text{C}$ -NMR (50 MHz,  $\text{CDCl}_3$ ) $\delta$ :

3.61 ( $\equiv\text{C}-\text{CH}_3$ ), 23.76 ( $\text{CH}-\text{CH}_3$ ), 55.87 ( $\text{OCH}_3$ ), 55.96 ( $\equiv\text{C}-\text{CH}_2\text{O}$ ),  
75.36 ( $\equiv\text{C}-\text{CH}_2$ ), 76.40 ( $\text{Ar}-\text{CH}-\text{CH}_3$ ), 81.91 ( $\equiv\text{C}-\text{CH}_3$ ), 109.06 (C-2),  
110.86 (C-5), 118.94 (C-6), 135.30 (C-1), 148.52 (C-3), 149.19 (C-4),

In an analogous way as described in Example 4.0 were prepared the following compounds:

	Compound	Mp( $^{\circ}\text{C}$ )	IR $\nu(\text{cm}^{-1})$	$^1\text{H}$ -NMR $\delta$ (ppm)	$^{13}\text{C}$ -NMR $\delta$ (ppm)
4.1 279	1-naphthyl- methyl 2-butyryl ether	oil	3044, 3001, 2945, 2920, 2854, 1598, 1509, 1356, 1166, 1086, 1067	1.93 (3H, t, $J=2.3$ Hz, $\text{C}\equiv\text{C}-\text{CH}_3$ ), 4.22 (2H, q, $J=2.1$ Hz, $\text{O}-\text{CH}_2-\text{C}\equiv\text{C}$ ), 5.06 (2H, s, $\text{C}_{10}\text{H}_7-$ $\text{CH}_2-\text{O}$ ), 7.45 (1H, t, $J=8$ Hz), 7.53 (3H, m), 7.84 (1H, d, $J=8.1$ Hz), 7.88 (3H, m), 7.88 (1H, d, $J=7.7$ Hz), 8.19 (1H, d, $J=8.2$ Hz)	3.6 ( $\text{C}\equiv\text{C}-\text{CH}_3$ ), 57.71 ( $\text{O}-\text{CH}_2-\text{C}\equiv\text{C}$ ), 69.72 ( $\text{C}_{10}\text{H}_7-\text{CH}_2-\text{O}$ ), 75.10 ( $\text{O}-\text{CH}_2-\text{C}\equiv\text{C}$ ), 82.76 ( $\text{O}-\text{CH}_2-\text{C}\equiv\text{C}$ ), 124.03, 125.10, 125.72, 126.19, 126.85, 128.43, 128.72, 131.79 (C-8a), 133.06, 133.70
4.2 292	1-[1-(2- butynyloxy)- ethyl]- naphthalene	oil	3052, 2977, 2921, 2856, 1596, 1509, 1444, 1371, 1095, 1078	1.67 (3H, d, $J=6.5$ Hz, $\text{CH}_3-\text{CH}$ ), 1.87 (3H, t, $J=2.3$ Hz, $\equiv\text{C}-\text{CH}_3$ ), 2.96 and 4.15 (summa 2H, ABX, $J_{\text{AB}}=15.0$ Hz, $J_{\text{AX}}=J_{\text{BX}}=2.3$ Hz, $\text{OCH}_2-\text{C}\equiv\text{C}$ ), 5.40 (1H, q, $J=6.5$ Hz, $\text{C}_{10}\text{H}_7-$ $\text{CH}-\text{O}$ ), 7.51 (3H, m), 7.61 (1H, d, $J=6.8$ Hz), 7.79 (1H, d, $J=8.1$ Hz), 7.89 (1H, dd, $J=7.9, 1.8$ Hz), 8.22 (1H, d, $J=8.1$ Hz)	3.64 ( $\text{C}\equiv\text{C}-\text{CH}_3$ ), 22.96 ( $\text{CH}_3-\text{CH}$ ), 56.37 ( $\text{O}-$ $\text{CH}_2-\text{C}\equiv\text{C}$ ), 74.29 ( $\text{CH}_3-$ $\text{CH}$ ), 75.36 and 82.14 ( $\text{C}\equiv\text{C}$ ), 123.26 (C-8), 123.52, 125.50, 125.85, 127.92, 128.83, 130.78 (C-8a), 133.88 (C-4a), 138.42 (C-1)



4.3 454	1-[1-(2-butynyloxy)-propyl]-naphthalene	oil	3058, 3048, 3000, 2962, 2932, 2923, 2876, 2856, 1598, 1509, 1460, 1105, 1062.	1.02 (3H, t, $J = 7.4$ Hz, $\text{CH}_3\text{-CH}_2$ ), 1.89 (3H, t, $J = 2.3$ Hz, $\text{C}\equiv\text{C-CH}_3$ ), 2.03 (2H, m, $\text{CH}_3\text{-CH}_2$ ), 3.95 and 4.17 (summa 2H, ABX, $J_{AB} = 15.0$ Hz, $J_{AX} = J_{BX} = 2.3$ Hz, $\text{OCH}_2\text{-C}\equiv\text{C}$ ), 5.15 (1H, t, $J = 6.4$ Hz, $\text{C}_{10}\text{H}_7\text{-CH-O}$ ), 7.53 (3H, m), 7.59 (1H, d), 7.81 (1H, d), 7.89 (3H, m), 8.27 (1H, d)	3.59 ( $\text{C}\equiv\text{C-CH}_3$ ), 10.62 ( $\text{CH}_3\text{-CH}_2$ ), 30.27 ( $\text{CH}_3\text{-CH}_2$ ), 56.54 ( $\text{O-CH}_2\text{-C}\equiv\text{C}$ ), 75.50 ( $\text{O-CH}_2\text{-C}\equiv\text{C}$ ), 80.08 and 81.96 ( $\text{OCH-naphthyl}$ and $\text{O-CH}_2\text{-C}\equiv\text{C}$ ), 123.43 (C-8), 124.40, 125.31, 125.36, 125.73, 127.91, 128.79, 131.19 (C-8a), 133.88 (C-4a), 137.12 (C-1)
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	Compound	Mp( $^{\circ}\text{C}$ )	IR $\nu$ ( $\text{cm}^{-1}$ )	$^1\text{H-NMR}$ $\delta$ (ppm)	$^{13}\text{C-NMR}$ $\delta$ (ppm)
4.4 472	1-[2-methyl-1-(2-butynyloxy)-propyl]-naphthalene	oil	3051, 2959, 2922, 2871, 1598, 1509, 1466, 1064.	0.87 and 1.16 (summa 6H, d each, $J = 6$ Hz, $\text{CH}(\text{CH}_3)_2$ ), 1.88 (3H, t, $J = 2.3$ Hz, $\text{C}\equiv\text{C-CH}_3$ ), 2.31 (1H, m, $\text{CH}(\text{CH}_3)_2$ ), 3.89 and 4.14 (2H summa ABX <sub>3</sub> , $J_{AB} = 15$ Hz, $J_{AX} = J_{BX} = 2.3$ Hz, $\text{OCH}_2$ ), 4.92 (1H, d, $J = 6$ Hz, $\text{CH-O}$ ), 7.53 (4H, m), 7.83 (1H, d, $J = 8$ Hz), 7.91 (1H, dd, $J = 7, 2$ Hz), 8.30 (1H, d, $J = 7.6$ Hz)	3.57 ( $\text{C}\equiv\text{C-CH}_3$ ), 19.87 and 18.77 ( $\text{CH}(\text{CH}_3)_2$ ), 34.20 ( $\text{CH}(\text{CH}_3)_2$ ), 56.71 ( $\text{OCH}_2$ ), 75.67 ( $\text{C}\equiv\text{C-CH}_3$ ), 81.77 ( $\text{C}\equiv\text{C-CH}_3$ ), 123.84 (C-8), 125.15, 125.31, 125.39, 125.60, 127.91 (C-4), 128.76 (C-5), 131.74 (C-8a), 133.87 (C-4a), 136.56 (C-1).

4.5 389	1-[(1-methyl-(2-propynyloxy)-methyl)-naphthalene	oil	3306, 3049, 2990, 2935, 2866, 1599, 1510, 1447, 1374, 1327, 1099, 1064	1.51 (3H, d, J=6 Hz), CH <sub>3</sub> ; 2.56 (1H, d, J=2 Hz), CH; 4.30 (H, qxd J=6.2 Hz) OCH; 4.91 and 5.34 (2H, AB, J <sub>AB</sub> = 15 Hz) OCH <sub>2</sub> ; 7.46 (1H, dd, J=7.8 Hz), 7.54 (3H, m), 7.86 (2H, m), 8.18 (1H, mxd, J=6 Hz) aromatic	22.1, CH <sub>3</sub> , 64.25, OCH; 68.99, CH; 73.34, aryl-CH <sub>2</sub> ; 83.71, CH-C; 124.11, C-8; 125.17, C-2; 125.74, C-3; 126.18, C-6; 126.92, C-7; 128.47, C-4; 128.75, C-5; 131.88, C-8a; 133.20, C-4a; 133.77, C-1
4.6 256	2-[1-(2-propynyloxy)-ethyl]-naphthalene	oil	3307, 3000, 2979, 2929, 2857, 1603, 1505, 1442, 1373, 1311, 1270, 1215, 1087, 1055, 860, 821, 633	1.58 (3H, d, J= 6.5 Hz, CH <sub>3</sub> -CH), 2.44 (1H, t, J=2.4 Hz) CH, 3.92 (1H, dd, J=2.4, 15.7 Hz) OCH <sub>a</sub> -C≡C, 4.13 (1H, dd, J=2.4, 15.7 Hz), OCH <sub>b</sub> -C≡C, 4.84 (1H, q, J=6.5 Hz, C <sub>10</sub> H <sub>7</sub> -CH-O), 7.50 (3H, m), 7.77 (1H, s), 7.85 (3H, m)	23.66 (CH <sub>3</sub> -CH), 55.55 (O-CH <sub>2</sub> -C≡C), 74.07 and 76.80 (CH-O, CCH), 79.98, (CCH), 124.11, (C-6), 125.60 (C-7), 125.90, 126.15, 127.68, 127.85, 128.5, 133.16, 133.21, 139.75 (C-1)
4.7 293	2-[1-(2-propynyloxy)-ethyl]-naphthalene	oil	3051, 2977, 2920, 2854, 1602, 1444, 1084	1.57 (3H, d, J= 6.5 Hz, CH <sub>3</sub> -CH), 1.87 (3H, t, J=2.3 Hz, CH <sub>3</sub> -C), 3.90 and 4.08 (1-1H, ABX3, J=15, 2.3 Hz, OCH <sub>a,b</sub> -C≡C), 4.79 (1H, q, J=6.5, C <sub>10</sub> H <sub>7</sub> -CH-O), 7.49 (3H, m), 7.77 (1H, bs, H-1), 7.85 (3H, m)	3.64 (C≡C-CH <sub>3</sub> ), 23.78 (CH <sub>3</sub> -CH), 56.23 (O-CH <sub>2</sub> -C≡C), 75.28 (C≡C-CH <sub>3</sub> ), 76.72 (CH-CH <sub>3</sub> ), 82.10 (C≡C-CH <sub>3</sub> ), 124.14, (C-6), 125.42, 125.78, 126.05, 127.64, 127.80, 128.40, 133.07 (C-4), 133.19 (C-8), 140.14 (C-2)

	Compound	Mp(C°)	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
5	4.8 441 5-[(But-2- ynyloxy)-methyl]- 1,3-benzodioxole	oil	2997, 2946, 2921, 2888, 2376, 1609, 1503, 1491, 1445, 1251, 1099, 1070, 1042, 937, 865, 810	1.87 (3H, t, J=2.3 Hz, Me), 4.10 (2H, q, J=2.3 Hz, O-CH <sub>2</sub> -C $\equiv$ ), 4.47, (2H, s, O-CH <sub>2</sub> -Ar), 5.94 (2H, s, O-CH <sub>2</sub> -O), 6.76 (1H, d, J=8 Hz, H-7), 6.81 (1H, dd, J=8.15 Hz, H-6), 6.86 (1H, J=1.5 Hz, H-4)	3.52 (Me), 57.29 (O-CH <sub>2</sub> -C $\equiv$ ), 71.15 (O-CH <sub>2</sub> -Ar), 82.54 (CH <sub>3</sub> -C $\equiv$ ), 100.9 C-2, 107.95, 108.71 (C-4,7), 121.66 (C-6), 131.39, (C-5), 147.15, 147.66 (C3a, C-7a)
15	4.9 484 5-[2-Methyl-1-(2- butynyloxy)- propyl]-1,3- benzodioxole	oil	2958, 2921, 2874, 1608, 1502, 1486, 1441, 1076, 1041, 940	0.63 and 0.94 (summa 6H, d each, J = 6.8 Hz, CH(CH <sub>3</sub> ) <sub>2</sub> ), 1.76 (3H, t, J = 2.3 Hz, C $\equiv$ -CH <sub>3</sub> ), 1.81 (1H, m, CH(CH <sub>3</sub> ) <sub>2</sub> ), 3.69 and 3.94 (summa 2H, ABX <sub>3</sub> , J <sub>AB</sub> =15.1 Hz, J <sub>AX</sub> = J <sub>BX</sub> = 2.3 Hz, OCH <sub>2</sub> ), 3.86 (1H, d, J = 7.8 Hz, CH-O), 5.87 (2H, AB, OCH <sub>2</sub> O), 6.62 (1H, dd, J = 7.9, 1.6 Hz, 6-H), 6.68 (1H, d, J = 7.9 Hz, 7-H), 6.71 (1H, d, J = 1.6 Hz, 4-H)	3.58 (C $\equiv$ C-CH <sub>3</sub> ), 18.93 and 19.30 ((CH(CH <sub>3</sub> ) <sub>2</sub> ), 34.42 (CH(CH <sub>3</sub> ) <sub>2</sub> ), 56.20 (OCH <sub>2</sub> ), 75.48 (C $\equiv$ C-CH <sub>3</sub> ), 81.66 (C $\equiv$ C-CH <sub>3</sub> ), 86.25 (CH-O), 100.85 (OCH <sub>2</sub> O), 107.44, 107.63 (C-4, 7), 121.29 (C-6), 134.48 (C-5), 146.88 and 147.63 (C-3a, 7a)

4.10 554	5-[(But-2- ynyloxy)- cyclohexyl- methyl]-1,3- benzodioxole	oil	2920, 2877, 2851, 1610, 1502, 1485, 1441, 1357, 1243, 1132, 1064, 1040, 942.	0.84-1.31 (6H, m), 1.50-1.77 (4H, m) 1.83 (3H, t, J=2.3 Hz, $\equiv$ C- CH <sub>3</sub> ), 2.08 (1H, m, H- 1'), 3.76 and 4.01 (ABX <sub>3</sub> , J <sub>AB</sub> =15 Hz, J <sub>AX</sub> =J <sub>BX</sub> =2.3 Hz, OCH <sub>2</sub> ), 3.98 (1H, d, J=8.3 Hz, CH-O), 5.97 (2H, s, OCH <sub>2</sub> O), 6.65- 6.78 (3H, m).	3.64 (C $\equiv$ C-CH <sub>3</sub> ), 25.93 and 26.05 (C-2', C-6'), 26.52 (C-3), 29.25 and 29.86 (C-3', C-5'), 43.97 (C-1'), 56.19 (OCH <sub>2</sub> ), 75.57 (C $\equiv$ C- CH <sub>3</sub> ), 81.64 (C $\equiv$ C- CH <sub>3</sub> ), 85.45 (CH-O), 100.88 (OCH <sub>2</sub> O), 107.47 and 107.64 (C- 4, C-7), 121.31 (C-6), 134.48 (C-5), 146.91 and 147.69 (C-3a, C- 7a).
4.11 555	5-[(But-2- ynyloxy)-phenyl- methyl]-1,3- benzodioxole	oil	2993, 2887, 2859, 1605, 1502, 1486, 1442, 1357, 1239, 1037, 937.	1.89 (3H, t, J=2.3 Hz, $\equiv$ C-CH <sub>3</sub> ), 4.12 (2H, q, J=2.3 Hz, OCH <sub>2</sub> ), 5.56 (1H, s, CH-O), 5.93 (2H, s, OCH <sub>2</sub> O), 6.74- 6.86 (3H, m), 7.25-7.39 (5H, m)	3.69 (C $\equiv$ C-CH <sub>3</sub> ), 56.34 (OCH <sub>2</sub> ), 75.12 (C $\equiv$ C- CH <sub>3</sub> ), 81.23 (C $\equiv$ C-CH <sub>3</sub> ), 82.56 (CH-O), 100.99 (OCH <sub>2</sub> O), 107.78 and 107.95 (C-4, C-7), 120.98 (C-6), 127.01 (C-2', C-6'), 127.50 (C- 4'), 128.36 (C-3', C-5'), 135.54 (C-5), 141.62 (C-1'), 147.05 and 147.83 (C-3a, C-7a)

## BEST AVAILABLE COPY

	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR δ (ppm)	<sup>13</sup> C-NMR δ (ppm)
5 10	4.12 493 (2-Butynyloxy- methyl)-3,4- dimethoxy- benzene	oil	3025, 3000, 2956, 2937, 2921, 2855, 2839, 1607, 1595, 1512, 1466, 1443, 1420, 1158, 1140, 1070, 1028	1.84 (3H, t, J=2.3 Hz, C≡C-CH <sub>3</sub> ), 3.83 and 3.85 (summa 6H, CH <sub>3</sub> O), 4.08 (2H, q, J=2.3 Hz, OCH <sub>2</sub> C≡C-), 4.48 (2H, s, aryl-CH <sub>2</sub> ), 6.77-6.88 (3H, m, aryl)	3.45 (C≡C-CH <sub>3</sub> ), 55.67 and 55.71 (CH <sub>3</sub> O), 57.31 (OCH <sub>2</sub> C≡C-), 71.22 (aryl-CH <sub>2</sub> ), 75.0 (C≡C-CH <sub>3</sub> ), 82.42 (C≡C-CH <sub>3</sub> ), 110.76 (C- 2), 111.23 (C-5), 120.54 (C-6), 130.05 (C-1), 148.58 (C-4), 148.88 (C-3).
15 20	4.13 503 2,6-Dichloro-1- (2-butynyloxy- methyl)- benzene	oil	2931, 2918, 2881, 2849, 2241, 1584, 1563, 1473, 1356, 1198, 1157, 1091, 1073, 787, 769	1.87 (3H, t, J=2.3 Hz, ≡C-CH <sub>3</sub> ), 4.21 (2H, q, J=2.3 Hz, OCH <sub>2</sub> -C≡), 4.83 (2H, s, C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> - O-CH <sub>2</sub> ), 7.17 (1H, dd, J=9.1, 6.7 Hz), 7.31 (2H, m)	3.64 (≡C-CH <sub>3</sub> ), 58.68 (OCH <sub>2</sub> -C≡), 66.15 (C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> -O-CH <sub>2</sub> ), 74.94 (OCH <sub>2</sub> -C≡), 82.81 (≡C-CH <sub>3</sub> ), 128.33 (C-3, C-5), 129.96 (C-4), 133.17 (C-2, C-6), 136.97 (C-1)
25 30	4.14 498 1-(2- Butynyloxy)- 1,2,3,4- tetrahydro- naphthalene	oil	2998, 2941, 2860, 1604, 1489, 1440, 1070, 1044	1.84 (3H, t, J=2.3 Hz, C≡C-CH <sub>3</sub> ), 3.83 and 3.85 (summa 6H, CH <sub>3</sub> O), 4.08 (2H, q, J=2.3 Hz, OCH <sub>2</sub> C≡C-), 4.48 (2H, s, aryl-CH <sub>2</sub> ), 6.77-6.88 (3H, m, aryl)	3.45 (C≡C-CH <sub>3</sub> ), 55.67 and 55.71 (CH <sub>3</sub> O), 57.31 (OCH <sub>2</sub> C≡C-), 71.22 (aryl-CH <sub>2</sub> ), 75.0 (C≡C-CH <sub>3</sub> ), 82.42 (C≡C-CH <sub>3</sub> ), 110.76 (C- 2), 111.23 (C-5), 120.54 (C-6), 130.05 (C-1), 148.58 (C-4), 148.88 (C-3)

4.15 479	1-(2- Butynyloxy)- indane	oil	3073, 3000, 2938, 2924, 2854, 2243, 1711, 1667, 1608, 1461, 1332, 1097, 1063, 1018	1.91 (3H, t, $J = 2.3$ Hz, $C \equiv C-CH_3$ ), 2.15 (1H, dddd, $J = 13.2, 8.4, 4.8,$ 3.8 Hz, 2-H), 2.37 (1H, dddd, $J = 15, 8.4, 6.5, 6.5$ Hz, 2-H), 2.83 (1H, ddd, $J = 15.8, 8.4, 4.8$ Hz, 3-H), 3.12 (1H, ddd, $J = 15, 7.2, 8.4, 3-$ H), 4.21 (2H, q, $J = 2.3$ Hz, $OCH_2$ ), 5.14 (1H, dd, $J = 6.5, 3.7$ Hz, 1-H), 7.23 (1H, m), 7.28 (2H, m), 7.45 (1H, d, $J = 7$ Hz).	3.52 ( $C \equiv C-CH_3$ ), 30.11 (C-2), 32.25 (C-3), 56.14 ( $OCH_2$ ), 75.45 ( $C \equiv C-CH_3$ ), 81.68 (C- 1), 82.15 ( $C \equiv C-CH_3$ ), 124.80, 125.16 (C-5,6), 126.11, 128.36 (C-4,7), 142.10, 144.14 (C- 3a,7a).
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	Compound	Mp(C°)	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
5	4.16 510 2-[(2-Butynyloxy)-methyl]-1,4-benzodioxane	oil	2996, 2921, 2858, 2222, 1594, 1492, 1466, 1269, 1097, 1043	1.87 (3H, t, J=2.4 Hz, C <sub>6</sub> H <sub>4</sub> ), 3.70 and 3.80 (2H, ABX, J <sub>AB</sub> =10.1 Hz, J <sub>AX</sub> =J <sub>BX</sub> =5.0 Hz, CH-CH <sub>2</sub> -O), 4.08 (1H, dd, J=7.6, 11.8 Hz, H-3 $\beta$ ), 4.20 (2H, d, J=2.3 Hz, O-CH <sub>2</sub> -C $\equiv$ ), 4.28-4.41 (2H, m, H-3 $\alpha$ , H-2 $\alpha$ ), 6.81-6.92 (4H, m, C <sub>6</sub> H <sub>4</sub> )	3.57 (H <sub>3</sub> C-C $\equiv$ ), 59.43 (O-CH <sub>2</sub> -C $\equiv$ ), 65.58 (CH-CH <sub>2</sub> -O), 68.12 (C-3), 71.96 (C-2), 74.54 (CH <sub>2</sub> -C $\equiv$ ), 83.22 (H <sub>3</sub> C-C $\equiv$ ), 117.12, 117.40 (C-5 and C-8), 121.37, 121.56 (C-6 and C-7), 143.07, 143.21 (C-4a, C-8a)
15	4.17 539 2-(2-butynyloxy-methyl)-2,3-dihydro-benzofuran	oil	3598, 3478 (broad), 3080, 3040, 2996, 2952, 2871, 1611, 1598, 1481, 1462, 1232, 1092, 1050, 1012, 1004, 954, 899, 865	2.65 (1H, t, J=5.4 Hz, OH), 2.97 and 3.25 (summa 2H, ABX, J <sub>AB</sub> =15.6 Hz, J <sub>AX</sub> =9.4 Hz, J <sub>BX</sub> =7.5 Hz, H-3), 3.79 (2H, m, CH <sub>2</sub> -OH), 4.90 (1H, m, H-2), 6.79 (1H, d, J=8.0 Hz), 6.87 (1H, td, J=7.5, 0.8 Hz), 7.11 (1H, d, J=7.8 Hz), 7.16 (td, J=7.2, 0.5 Hz)	31.18 (C-3), 64.77 (CH <sub>2</sub> -OH), 83.02 (C-2), 109.36 (C-7), 120.54 (C-5), 124.97 (C-6), 126.48 (C-3a), 127.95 (C-4), 159.08 (C-7a)
20					
25					

	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	$[\alpha]_D^{20}$
5	4.18 330 S-(-)-1-[1-(2-butynyloxy)-ethyl]-naphthalene	oil	like 4.2 292	(-) 78° (c=1, MeOH)
	4.19 331 R-(+)-1-[1-(2-butynyloxy)-ethyl]-naphthalene	oil	like 4.2 292	(+) 155° (c=1, chloroform)
10	4.20 456 S-(-)-2-[1-(2-butynyloxy)-ethyl]-naphthalene	oil	like 4.7 293	(-) 190.8° (c=1.0, chloroform)
	4.21 455 R-(+)-2-[1-(2-butynyloxy)-ethyl]-naphthalene	oil	like 4.7 293	(+) 199.0° (c=1.17, chloroform)
15	4.22 474 S-(-)-2-[1-(2-propynyloxy)-ethyl]-naphthalene	oil	like 4.6 256	(-) 224.4° (c=1.18, chloroform)
20	4.23 475 R-(+)-2-[1-(2-propynyloxy)-ethyl]-naphthalene	28-29	like 4.6 256	(+) 228° (c=1, chloroform)



## 5. Aromatic alkyl-alkynyl-amine derivatives

## General procedure

The amine was dissolved in dry benzene, the alkynyl bromide was added and the mixture was stirred at room temperature. Then it was diluted with water and ether, the phases were separated, the aqueous phase was twice extracted with ether, the combined organic phases were washed with water, and dried on  $\text{MgSO}_4$ .

	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
5.1 251	N- $\alpha$ -dimethyl- N-2-propynyl- $\beta$ -naphthyl- methylamine	51-53	3173, 3053, 2970, 2941, 2837, 2788, 1600, 1444, 1433, 1371, 1334, 1295, 1227, 1123, 1074, 1011, 969, 952, 935, 900, 863, 827, 754, 734, 713, 557, 482	1.455 (3H, d, CH-Me), 2.271 (1H, s, CCH), 2.360 (3H, s, NMe), 3.253-3.302 and 3.487-3.530 (2H, CH <sub>2</sub> ), 3.708-3.757 (1H, m, CHMe), 7.260-7.834 (7H, m, aromatic)	

## 6. Aryl alkynyl ethers

## General procedure

## 5 A.)

The appropriate phenol was dissolved in dry DMF and to the solution dry  $K_2CO_3$  and the appropriate alkynyl halogenide were added. The reaction mixture was heated to 60°C and stirred at that temperature for 3-6 hours. DMF was then distilled off in vacuo, the residue was taken up in the mixture of  
10 chloroform and distilled water. The phases were separated, the aqueous phase was twice extracted with chloroform, the combined organic phases were washed consecutively with water and saturated sodium chloride solution, dried on  $MgSO_4$  and evaporated. The raw product was purified by chromatography.

## 15 B.)

$Ph_3P$  was dissolved in dry benzene in an inert atmosphere and to the solution the appropriate alcohol and then the phenol were added. The mixture was cooled to 0-10°C, and DEAD (diethyl-azo-dicarboxylate) was added slowly, in small portions, keeping the temperature below 10°C. The reaction mixture was  
20 stirred for 10-24 hours.

Work-up: the precipitated  $Ph_3PO$  was filtered off, the filtrate was washed with water, dried and evaporated. The residue was chromatographed.

## 25 C.)

0.01 mol of phenol were dissolved in 7 ml of dry acetonitrile and under argon atmosphere it was cooled to -4 °C. To the solution were then added 1.968g (0.0129 mol) DBU, keeping the temperature below -4 °C. To the resulting solution 1.8g copper(II)-chloride were added and paralelly the trifluoroacetate  
30 of the other reactant was prepared.

0.0115 mol alkynyl-alcohol were dissolved in 7 ml of acetonitrile, and the solution was cooled to  $-5^{\circ}\text{C}$ , under argon atmosphere. To the solution were added 1.968g (0.0129 mol) DBU, while keeping the temperature below  $-5^{\circ}\text{C}$ . To the mixture were added dropwise 1.6g (0.0115mol) trifluoroacetic  
5 anhydride, keeping the temperature below  $2^{\circ}\text{C}$ . The resulting mixture was stirred at  $0^{\circ}\text{C}$  for 30 mins.

The trifluoroacetate solution thus obtained was added dropwise to the first solution, keeping the temperature below  $0^{\circ}\text{C}$  and the mixture was stirred at  $0^{\circ}\text{C}$  for 5 hours. The reaction was followed by TLC. At the end of the reaction  
10 the acetonitrile was distilled off in vacuo. The residue was shaken with the mixture of 150 ml of benzene and 50 ml of water. The organic layer was washed consecutively with 1N hydrochloric acid, 1N sodium hydroxide, water and saturated sodium chloride solution, then dried and evaporated. The product was purified by chromatography.

15

	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR δ (ppm)	<sup>13</sup> C-NMR δ (ppm)
5	6.1 547 1-(3-butynyloxy)- 4-nitro-benzene	92-94	3287, 3111, 3085, 3075, 2964, 2947, 2920, 1609, 1596, 1510, 1466, 1344, 1333, 1263, 1179, 1110, 1019, 856, 846, 753, 669, 653.	2.07 (1H, t, J=2.6 Hz, C≡C-H), 2.73 (2H, td, J=6.8, 2.6 Hz, CH <sub>2</sub> C≡C), 4.18 (2H, t, J=6.8 Hz, OCH <sub>2</sub> ), 6.97 and 8.18 (summa 4H, dm, J=9 Hz, C <sub>6</sub> H <sub>4</sub> )	19.37 (C≡C-CH <sub>2</sub> ), 66.60 (C≡CH), 70.38 (OCH <sub>2</sub> ), 79.62 (C≡CH), 114.51 (C-2, C-6), 125.89 (C-3, C-5), 141.73 (C-4), 163.40 (C-1)
10	6.2 540 1-(3-pentynyloxy)-4- nitro-benzene	77-78	3067, 3048, 2963, 2917, 2886, 1923, 1607, 1594, 1512, 1467, 1403, 1339, 1260, 1178, 1110, 866, 856, 753, 694, 648, 628, 522, 506.	1.78 (3H, t, J=2.3 Hz, C≡C-CH <sub>3</sub> ), 2.66 (2H, m, CH <sub>2</sub> C≡C), 4.12 (2H, t, J=7.0 Hz, OCH <sub>2</sub> ), 6.95 and 8.18 (summa 4H, dm, J=9 Hz, C <sub>6</sub> H <sub>4</sub> )	3.57 (C≡C-CH <sub>3</sub> ), 19.61 (C≡C-CH <sub>2</sub> ), 67.26 (OCH <sub>2</sub> ), 74.27 (C≡C- CH <sub>3</sub> ), 77.84 (C≡C- CH <sub>3</sub> ), 114.49 (C-2, C- 6), 125.85 (C-3, C-5), 141.59 (C-4), 163.59 (C-1).
20	6.3 377 2,3-dihydro, 2,2- dimethyl-7-(3- butynyloxy)- benzofuran	78-80	3277, 3071, 3043, 2970, 2923, 2889, 2858, 2119, 2022, 1874, 1795, 1714, 1656, 1624, 1611, 1591, 1492, 1470, 1440, 1492, 1396, 1385, 1371, 1302, 1283, 1244, 1201, 1172, 1128, 1077, 999, 972, 946, 887, 838, 780, 753, 720, 682, 663, 635, 600, 546, 502, 458	1.512 (6H, s, diMe), 2.033 (1H, t, CH), 2.710 (2H, m, -CH <sub>2</sub> C), 3.027 (2H, s, CH <sub>2</sub> -ar), 4.206 (2H, t, O-CH <sub>2</sub> ), 6.739-6.815 (3H, m, aromatic)	19.12 (CH <sub>2</sub> -C), 27.88 (diMe), 42.93 (C-3), 66.79 (C-2), 69.61 (O- CH <sub>2</sub> ), 79.96 (CCH), 87.06 (CC), 113.31 (C- 6), 117.86 (C-5), 119.99 (C-4), 128.36 (C-9), 142.62 (C-7), 147.52 (C-8)
25					
30					

6.4 418	2,3-dihydro- 2,2- dimethyl-7-(3- pentynyloxy)- benzofuran	58-59.5	2977, 2963, 2942, 2918, 2880, 2849, 1621, 1591, 1492, 1468, 1389, 1369, 1329, 1305, 1286, 1245, 1203, 1174, 1135, 1115, 1080, 1065, 966, 947, 881, 860, 841, 779, 751, 718, 634, 598, 532, 499.	1.510 (6H, s, diMe), 1.800 (3H, t, Me), 2.627-2.672 (2H, m, - CH2C), 3.023 (2H, s, CH2-ar), 4.150 (2H, t, O-CH2), 6.751-6.784 (3H, m, aromatic)	3.471 (Me), 19.63 (CH2-C), 28.18 (diMe), 43.26 (C-3), 67.54 (C- 2), 74.82 (CC-Me), 77.32 (O-CH2), 87.26 (CC), 113.21 (C-6), 117.87 (C-5), 120.25 (C-4), 128.48 (C-9), 143.12 (C-7), 145.00 (C-8)
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## 7. Alkynyl-oxim-ethers

## General procedure

The oxime was transformed to the oxim-ether in the classical way, by reacting it with the alkynyl bromide in dimethyl formamide, in the presence of potassium carbonate (See method A under the preparation of naphthyl ethers). The raw product was in each case purified by column chromatography.

	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR δ (ppm)	<sup>13</sup> C-NMR δ (ppm)
7.1 571	1-Aceto-naphthon-oxim-(2-butyryl)-ether	oil	2990, 2919, 2853, 2230, 1604, 1591, 1459, 1436, 1363, 1353, 1309, 1252, 1034, 1017, 1002, 912	1.94 (3H, t, J=2.3 Hz, CH <sub>3</sub> -C≡), 2.41 (3H, s, CH <sub>3</sub> -C=N), 4.84 (2H, q, J=2.3 Hz, O-CH <sub>2</sub> ), 7.46-7.57 (4H, m), 7.87 (2H, m), 8.15 (1H, m)	3.80 (CH <sub>3</sub> -C≡), 17.51 (CH <sub>3</sub> -C=N), 62.25 (O-CH <sub>2</sub> ), 75.33 (CH <sub>2</sub> -C≡), 82.75 (CH <sub>3</sub> -C≡), 125.15, 125.46 (C-6, C-7), 125.96 (C-3), 126.01 (C-3), 126.49 (C-2), 128.40 (C-5), 129.10 (C-4), 130.85 (C-1), 133.86 (C-4a), 135.27 (C-8a), 157.41 (CH <sub>3</sub> -C=N)
7.2 572	3,4-Dimethoxy-acetophenonoxym-(2-butyryl)-ether	85	3080, 3003, 2963, 2929, 2869, 2840, 2237, 1595, 1577, 1518, 1447, 1417, 1337, 1311, 1278, 1249, 1234, 1176, 1153, 1030, 937, 879, 804, 768, 634, 621	1.87 (3H, t, J=2.3 Hz, CH <sub>3</sub> -C≡), 2.23 (3H, s, CH <sub>3</sub> -C=N), 3.88 and 3.90 (CH <sub>3</sub> O), 4.75 (2H, q, J=2.3 Hz, O-CH <sub>2</sub> ), 6.83 (1H, d, J=8.4 Hz), 7.15 (1H, dd, J=8.4, 2 Hz), 7.29 (1H, d, J=2 Hz)	3.77 (CH <sub>3</sub> -C≡), 12.76 (CH <sub>3</sub> -C=N), 55.86 (CH <sub>3</sub> O), 62.23 (O-CH <sub>2</sub> ), 75.27 (CH <sub>2</sub> -C≡), 82.53 (CH <sub>3</sub> -C≡), 108.8 (C-5), 110.51 (C-2), 119.28 (C-6), 129.18 (C-1), 148.78 (C-3), 150.14 (C-4), 155.0 (CH <sub>3</sub> -C=N)

Activity results:**BEST AVAILABLE COPY**Example 1.

Investigation of synergistic activity on house fly (*Musca domestica*) following topical application

In two parallel experiments 10 female, 2-4 day old house flies were treated on the ventral side of their thorax with 0.2  $\mu$ l of the test solution, with the help of Hamilton MicroLab P microdispenser. Beside *fixed synergist dose of 1000 ng/fly* the animals were treated with carbofuran at a dose of 20 ng/fly. For solvent cellosolve was used. Selection and counting of the flies were performed under the action of CO<sub>2</sub>. After treatment the flies were kept in plastic cups covered with tulle. Mortality after 24 hours was expressed in %. Results are demonstrated in the table below:

Material	Carbofuran+synergist (ng/fly)	
	20+0	20-1000
	mortality %	
<i>Alkynyl esters, amides, imides</i>		
501	3	53
502	0	47
523	0	17
535	3	27
541	0	46
542	0	42
<i>Aryl- alkyl- alkynyl ethers</i>		
279	0	72
256	0	32
441	1	97
484	0	63
493	1	100
599	10	100
503	0	95
292	0	72
293	0	45

5	454	0	75
	472	1	68
	479	1	58
	330	0	62
	331	0	72
	455	0	70
	456	0	47
	389	2	27
	554	0	58
10	555	0	90
	539	0	48
	474	0	50
	510	2	75
	498	5	70
15	475	0	47
	Aromatic alkyl- alkyl-alkynyl- amine derivatives		
	251	2	37
	Aryl alkynyl ethers		
	547	0	47
20	540	0	60
	377	0	57
	418	0	63
	Aralkyl-aldoxime, ketoxime-alkynyl ethers		
	571	0	53
25	572	0	55

### Example 2.

Investigation of synergistic activity on cotton bollworm (*Helicoverpa armigera*) following topical application

Treatment was performed similarly as described in Example 1. but L2 stadium grubs of cotton bollworms (*Helicoverpa armigera*) were treated as test animals. From the 24 hour dose - mortality data the LD<sub>50</sub> (ng/grub) values were



determined using probit analysis. None of the synergists acted at the applied 1000 ng/grub dose. Synergist ratio was calculated as the quotient of the LD<sub>50</sub> values of carbofuran administered alone, and with the synergist. The experiments were performed in 2-4 replica. Synergist ratios are demonstrated in the table below:

Materials	Synergist ratio
<i>Alkynyl-esters, amides</i> 501, 502, 523, 535, 541, 542, 537	>5
<i>Aryl-alkyl alkyl-alkynyl ethers</i> 279, 256, 441, 484, 493, 503, 292, 293, 454, 510, 475, 498, 479, 472, 331, 455, 456, 389, 554, 555, 539, 474, 330, 599	>5
<i>Aromatic alkyl- alkyl-alkynyl-amine derivatives</i> 251	>5
<i>Aryl alkynyl ethers</i> 540, 377, 418	>5
<i>Alkynyl-oximethers</i> 571 572	>5

### Example 3.

Investigation of synergist spectrum on house fly (*Musca domestica*) and cotton bollworm (*Helicoverpa armigera*) following topical administration

Synergistic activities of materials No. 279 and 599 of the present invention for various active ingredients were determined on house fly (*Musca domestica*) and cotton bollworm (*Helicoverpa armigera*) using methods of treatments as described in biological Examples 1 and 2. For the active ingredients ISO

common names are given (see: Pesticide Manual 1994). The obtained synergist ratios are shown below:

5	active ingredient	279		599	
		Musca domestica	Helicoverpa armigera	Musca domestica	Helicoverpa armigera
10		Synergist ratio		Synergist ratio	
	carbofuran	>20	>10	>40	>20
	bendiocarb	>20	>10	>40	>20
	isoprocarb	>40	-	>40	>20
	fenobucarb	>10	-	>20	-
	aminocarb	>20	-	>20	-
	thiodicarb	>10	-	>10	-
	methomyl	>10	-	>10	-
15	pirimicarb	>20	-	>20	-
	dioxacarb	>20	-	>40	>20
	propoxur	>20	>10	>40	>20
	imidacloprid	>5	-	>5	-
	lindan	>5	>5	-	-
20	azinphosmethyl	>5	>5	-	-
	chlorpyrifos	>5	>5	-	-
	esbiol	>5	-	>10	-
	permethrin			>5	>10
	tetramethrin			>5	-

Example 4.

Effect of the active ingredient:synergist ratio on the synergistic activity

Treatment was performed as described in Example 1. using Hamilton MicroLab P microdispenser. In two parallel experiments 10 female, 2-3 day old flies were treated on the ventral side of their thorax with 0.2 µl test solution. Beside 1000-400-200-80 ng/fly fixed doses of the synergist they were treated with *constant* 20 ng/fly carbofuran. Selection and counting of the flies were performed under the action of CO<sub>2</sub>. After treatment the flies were kept in plastic cups covered with tulle. After 24 hours mortality % was recorded. Depending on the results the experiments were performed in 2-4 replica. Results are demonstrated in the table below.

Materials	Dose of the Synergist (ng/fly)				
	0	80	200	400	1000
	24 hour mortality (%)				
501	0	60	75	80	80
441	0	62	67	90	95
493	0	75	88	94	100
503	0	37	50	65	93
454	0	40	45	60	75
455	0	25	48	63	77
599	0	65	90	95	100

Example 5.

Investigation of synergistic activity on resistant house fly (*Musca domestica*) populations

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The table below demonstrates synergistic activities of materials of the present invention for various active ingredients on two resistant house fly strains (INSEL, IX). Investigation was carried out as described in biological Example 1. LD<sub>50</sub> values and synergist ratios were determined as given in Example 2.

10

Treatment	INSEL strain		IX strain	
	LD <sub>50</sub> (ng/fly)	SR	LD <sub>50</sub> (ng/fly)	SR
carbofuran	15375		>100000	
+ 279	29	530	94	4760
methomyl	475		851	
+ 279	46	10	109	5
pirimicarb	>100000		>100000	
+ 279	696	145	3562	115
aldicarb	695		2104	
+ 279	172	4	507	4
bendiocarb	100000		100000	
+ 279	150	667	746	134
isoprocarb	>100000		>100000	
+ 279	983	102	2145	47
esbiol	10653		-	
+ 279	794	13	-	-

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20

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Example 6.

Investigation of synergistic activity on oat aphid (*Rhopalosiphum padi*)

5 5-8 cm high oat plants, sawn in plastic cups were infected with different aged specimens of *Rhopalosiphum padi* aphids. The settled aphids were counted before the treatment, then the plants were sprayed, using a hand sprayer, with 1 ml of the spray solution, beside the *administration of fixed dose (30 ppm) of the synergist*. Of compound No. 279 of the present invention a 100 g/l  
10 concentration emulgeable concentrate was prepared, by methods usual in the formulation praxis, applying solvent and surface active materials. Test solutions used for the spraying were prepared from this concentrate and from marketed preparations by dilution. Mortality of the aphids was determined 24 hours after the treatment. Results are shown below:

15

Treatment	Mortality %
carbofuran 1 ppm	<.50
carbofuran 1 ppm + 279	> 95
pirimor 2 ppm	< 30
20 pirimor 2 ppm + 279	> 95
imidacloprid 0.1 ppm	< 50
imidacloprid 0.1 ppm - 279	> 95

Example 7.

25 Investigation of the effect on fecundity, on house fly (*Musca domestica*)

Groups consisting of freshly hatched 50 male and 50 female flies were fed during 48 hours with granulated sugar comprising 500 ppm of material No. 441  
30 and 484 of the present invention respectively, and the eggs layed on the next 10 days were raised. The fecundity-hindering effect was expressed as the quotient

of the emerged flies in the treated and untreated groups. The experiments were performed in 4 replica.

Treatment	Hindering effect on fecundity
441	87 %
484	90 %

### Example 8.

Synergism of acaricidal effect investigated on two-spotted spider mite (*Tetranychus urticae*)

From the first pair of leaves of a 1 week old bean plant leaf-discs of 225 mm diameter were cut which were treated by dipping them (5 min) into the test solution consisting of the active ingredient and the synergist in definite concentrations. For the preparation of the stock solutions of required concentration, 10 % acetone as co-solvent and 0.1 % Tween-80 as detergent were applied. The dried leaf-discs were placed on wet surface and they were infected with 10 grown-up female mites per leaf. After 48 hours the mortality was recorded using microscope and a brush. The experiment was performed in 4 replica. Averages of the results are shown in the table below.

Treatment with the active ingredients alone	Concentration (ppm)				
	31	62	125	250	500
	Mortality %				
279	0	6	8	18	30
carbofuran	13	39	44	81	90
bromopropylate	18	28	90	-	-
Treatment with the active ingredients in combinations	Concentration (ppm)				
	16+16	31+31	62+62	125+125	250+250
	Mortality %				
279+carbofuran	29	80	80	100	100
279+bromopropylate	75	90	100	-	-

Example 9.

Efficacy in field trial against Colorado potato beetle (*Leptinotarsa decemlineata*)

Of compound No. 279 of the present invention a 100 g/l concentration emulgeable concentrate was prepared by methods usual in the formulation praxis, applying solvent and surface active materials. Chinufur 40 FW composition, comprising 400 g/l carbofuran was applied together with a fixed dose of 2 l/ha of compound No. 279, in a small plot field study against Colorado potato beetle (*Leptinotarsa decemlineata*). Spraying was carried out with motoric sprayer (Maruyama) applying 300 l/ha spray solution. Treatments were performed in 4 replica, on plots of 25 m<sup>2</sup>. The effect of the treatments was evaluated on the 2nd day by counting the surviving beetles on the plants. Results are shown in the table below:

Treatment	Dose (l/acre)	carbofuran:279 ratio	Number of potato beetles piece/plant	
			before treatment	after treatment
untreated	-	-	23.6	28.0
Chinufur 40 FW	0.1	1:0	18.4	6.1
Chinufur 40 FW	0.2	1:0	32.0	6.8
Chinufur 40 FW+279	0.1+2.0	1:5	21.3	0.4

Example 10.

## Synergist activity of compound Nr. 599

Synergist activity of compound 599 with various specific acaricides was investigated against two-spotted spider mite (*Tetranychus urticae*), by the method described in Example 8. The  $LC_{50}$  and  $LC_{95}$  values calculated from the concentration-mortality relationship are shown in the table below.

Synergist activity against two-spotted spider mite (*Tetranychus urticae*)

Treatment	Ratio of Acaricide/ Synergist	Exposure time (h)	$LC_{50}$	$LC_{95}$	Synergist ratio	
			(mg)	(/l)	$SR_{50}$	$SR_{95}$
Carbofuran	1:0	24	163.9	799.9	-	-
Carbofuran+MB-599	1:1	24	55.5	286.8	3.0	2.8
	1:2	24	33.5	93.7	4.9	8.5
	1:4	24	27.5	67.0	6.0	11.9
Fenazaquin	1:0	3	>1000	-	-	-
	1:0	24	41.9	801.3	-	-
Fenazaquin + PBO	1:1	3	326.7	>1000	>3.1	-
	1:1	24	20.4	371.8	2.1	2.2
Fenazaquin+MB-599	1:1	3	68.1	280.2	>15	-
	1:1	24	31.3	174.8	1.3	4.6
Tebufenpyrad	1:0	3	>1000	-	-	-
	1:0	24	63.4	>1000	-	-
Tebufenpyrad +PBO	1:1	3	115.9	1081	>9	-
	1:1	24	35.7	118.0	1.8	>8.5
Tebufenpyrad+MB599	1:1	3	61.8	658.7	>16	-
	1:1	24	22.3	141.8	2.8	>7.0



Example 11.Synergist activity against pea aphid (*Acyrtosiphon pisum*)

Synergist activity of compound No. 599 was tested against pea aphid (*Acyrtosiphon pisum*) in field trials on small plots (10 m<sup>2</sup>). 300 l/ha spray volume was applied using motoric sprayer (Maruyama). Efficacy was expressed by the average number of aphids/leaf before, and two days after the treatment, respectively. (Henderson and Tilton: J. Econ. Entomol., 48:157, 1955). Results are shown in the table below.

Treatment	Dose act. ingr./ha.	E (%)
Pirimicarb	250	93.8
	80	86.3
Pirimicarb + MB-599	80+80	95.5
Fipronil	240	94.6
Fipronil + MB-599	120+120	95.7
Carbofuran	160	99.1
	110	98.0
Carbofuran + MB-599	110+110	100.0
Triazamate	50	96.8
Triazamate + MB-599	33+33	97.7
Imidacloprid	120	98.4
Imidacloprid+MB-599	120+120	100.0

Example 12.

## Comparative investigations with known reference synergists

LD<sub>50</sub> values of the reference compounds were determined in 4 replica on flies treated with carbofuran and 1000 ng of the known synergist, and the SR<sub>50</sub> ratios were counted in relation to the control carbofuran. These SR<sub>50</sub> ratios were

compared to those of the new compounds prepared by us. Our compounds were more active in each case.

1. Alkynyl esters

known

according to the  
invention

Synergist ratio	2-propynyl 1-naphthyl-carboxylate	502
SR <sub>50</sub>	4.11	6.28

2. (Aryl-alkyl), alkyl-alkynyl ethers

known

according to the  
invention

Synergist ratio	(2,6-dichlorophenyl)methyl 2-propynyl ether	503
SR <sub>50</sub>	20.92	21.16

known

according to the  
invention

Synergist ratio	5-[(2-propynyl)-methyl]-1,3-benzodioxole	441
SR <sub>50</sub>	10.60	25.70

known

according to the  
invention

Synergist ratio	1-naphthylmethyl 2-propynyl ether	279
SR <sub>50</sub>	5.28	28.7

known

according to the  
invention

Synergist ratio	2-[(2-propynyloxy)methyl]-1,4-benzodioxane	510
SR <sub>50</sub>	5.58	18.32

known

according to the  
invention

Synergist ratio	(2-propynyloxy-methyl)-3,4-dimethoxy-benzene	493
SR <sub>50</sub>	6.58	32.84

## 3. Aryl alkynyl ethers

known

according to the  
invention

Synergist ratio	2,3-dihydro-2,2-dimethyl-7-(2-propynyloxy)benzofurane	418
SR <sub>50</sub>	1.8	20.5

Known naphthyl alkynyl ether	Synergist ratio SR <sub>50</sub>
1-naphthyl 2-propargyl ether	6.52
1-naphthyl 3-butynyl ether	7.95
2-naphthyl 2-butynyl ether	7.72
2-naphthyl 3-pentynyl ether	9.97

## 4. Alkynyl-oxim-ethers

known

according to the  
invention

Synergist ratio	1-acetonaphthon-oxim (2-propynyl) ether	571
SR <sub>50</sub>	7.79	10.02

Examples for formulation:

Names of the marketed auxiliary materials are given in quotation marks, followed by the makers name.

5

## 1. Preparation of powders

## A)

To 158g of fine-grained perlite 20g of carbofuran and 20g of compound 279, were mixed in a homogenizator to this mixture were added 2g of fatty alcohol polyglycol ether ("G-3920" ICI) and the mixture was homogenized. The powder mixture was grained in an ejector mill and to it were added 5g of octyl-phenol-polyglycol-ether (EO=20) ("Triton X-165" Rohm & Haas) and 2g of alkyl-sulfosuccinate ("Aerosol-13" Cyanamid). The resulting product is a wettable powder mixture (WP).

15

## B)

10g of compound 279 and 10g of carbofuran were diluted with 2g of ethanol. The solution was mixed in a powder homogenisator with 5g of calcium-lignin-sulfonate ("Borrespeseca" Borregard), 5g of nonyl-phenol-polyglycol-ether (EO=20) ("Arkopal N-200" Hoechst), and 70g of calcium carbonate. The resulting product was grained in an alpine-100 typ mill. Average particle size was 1-2  $\mu\text{m}$ . This composition may be used to prepare microsupensions.

25

## C)

The mixture of 3g of Diazinon, 3g of compound 441, and 0.3g of fatty alcohol-polyglycol-ether ("G-3920" ICI) was taken up in a homogenisator apparatus on the mixture of 1.0g synthetic silicic acid (Aerosil 200) and 191g talc ( $d_{\text{max.}}=15-30 \mu\text{m}$ ), the pH of the latter was previously adjusted to pH=7.0 with potassium-

30

and sodium-phosphate buffer. Under further stirring 1g of dioctyl-sulfo-succinate ("Aerosol OTB" Cyanamid) and 1g of fatty alcohol-polyglycol-ether-sulfonate ("Genapol LRD" Hoechst) were added and finally the mixture was grained to an average particle size of 20  $\mu\text{m}$ . The resulting product is an easy  
5 flowing powder preparation.

## 2. Preparation of emulsion concentrates

### 10 A)

The mixture of 5g of pirimicarb and 5g of compound 493 was dissolved in the mixture of 20g of xylene and 40g of propanol. To this solution was added the mixture of 4g of ethoxylated alkyl-phenol + lineare alkyl-aryl-sulfonate-calcium salt ("Geronol FF/U Geronazzo) and 6g of ethoxylated amine + fatty acid +  
15 lineare alkyl-aryl-sulfonate alkali metal salt ("Geronol MS" Geronazzo). After complete dissolution 20g of water were added. Transparent solution was obtained, for which is characteristic, that on dilution with water it forms an emulsion of 0.8-1.5  $\mu\text{m}$  drop-diameter.

### 20 B)

The mixture of 5g of quinalphos and 10g of compound 484 and the mixture of 7g of ethoxylated-(EO=13)-propoxylated-(PO=21)-nonylphenol, 2g of lineare-dodecylbenzenesulfonic acid-calcium salt and 12g POE-(20)-sorbitan-monooleate were dissolved in the mixture of 28.6-28.6 ml of propyleneglycol  
25 and pine-fatty acid and 23.8ml of sun-flower oil, 9.5ml of etanol and 95 ml of aliphatic hydrocarbone with 45% naphthene content. The material thus obtained may be preferably used for the preparation of microemulsions.

### C)

30 The mixture of 0.02-0.02 parts by mass of the active ingredient and of the synergist is dissolved in 10 parts by mass of propanol. to the resulting solution

99.96 parts by mass of odourless petroleum are added and the mixture is stirred until a homogenous solution is obtained. The resulting oily dispersible preparation can directly be used in ULV applications.

5 D)

The method described in example A) is followed, with the difference that 10g of compound 279 is applied as synergist active ingredient.

10 3. Preparation of granulates

In a mechanical granulator are mixed 300g of carbofuran, 300g of compound 418, 1500g of polycarboxylate alkali salt ("Sorphol." Toho), 500g of dodecylbenzenesulfonic acid sodium salt ("Marlon TP 370" Hüls), 500g of beet sugar and 7200g of caolinite. The powder mixture thus obtained is mixed with 8300ml of water using a mixer of high shear force ( $v=10\text{m/s}$ ). The mixture is finally spray-dried. Particle-size distribution of the product is 0.1-0.4 mm.

4. Preparation of aerosols

20

In a 100 l apparatus supplied with stirrer are mixed 1kg of bioallethrin, 0.5kg of compound 441, 0.1kg of aerosil-air 972, 0.1 kg of ethyleneglycol-monosalicylate, 15kg of odourless petroleum and 50kg of propanol. After dissolution it is filled into cylinders with 33.3kg of liquid propane-butane

25 (25-75) gas.

## 5. Preparation of vaporators

In 60 ml of ethanol are dissolved 5g of S-bioallethrin, 5g of compound 279 and 1 g of lemon aroma. The solution is applied in vaporators. at a temperature of 50 °C.

**What we claim is:**

1.) Compounds of the general formula I . their optically active isomers and salts  
- wherein

- 5 Ar = alycyclic, aromatic or one or more heteroatom containing heterocyclic moiety. optionally substituted by one or more alkoxy-, methylenedioxy-, alkyl-, halogen-, haloalkyl-, or nitro-group and/or condensed with a benzene ring;  
R<sup>1</sup>, R<sup>2</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl.
- 10 R<sup>3</sup>, R<sup>4</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, or  
R<sup>3</sup>, R<sup>4</sup> are together =O,  
Y = C; PO, or
- 15 YR<sup>3</sup>R<sup>4</sup> together  $\begin{array}{c} \text{R}^9 \\ | \\ -\text{C}=\text{N}- \end{array}$  group;  
X = -O-; -NR<sup>10</sup>;  
R<sup>9</sup> = H, alkyl, phenyl, substituted phenyl;  
R<sup>10</sup> = H, alkyl;  
R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> are independently H, alkyl, alkenyl, haloalkyl, or
- 20 Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(YR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X- form together a carboximide group;  
E = H, halogen, methyl;  
m = 0, 1, 2 ;  
n = 0, 1 ;  
o = 0, 1, 2 ;
- 25 p = 0, 1, 2.
- with the proviso, that the sum of the atoms or groups of the -(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X-(CR<sup>5</sup>R<sup>6</sup>)<sub>o</sub>-(CR<sup>7</sup>R<sup>8</sup>)<sub>p</sub> bridge skeleton is 3 and the -C≡C-E skeleton forms with the atoms of the bridge a linear chain, consisting of 6 atoms ending preferably in a methyl group,



furthermore with the proviso, that if Ar stands for a naphthyl group. Y means C-atom. X means O-atom. R<sup>3</sup> and R<sup>4</sup> together can not mean =O.

2.) Compounds of general formula IA and their optically active isomers - where  
5 Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o and p have the same meanings as defined in claim 1.

3.) Compounds of general formula IB and their optically active isomers - where  
10 Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, Y, E, m, o and p have the same meanings as defined in claim 1.

4.) Compounds of general formula IC and their optically active isomers - where  
15 Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o and p have the same meanings as defined in claim 1.

5.) Compounds of general formula ID and their salts and optically active  
isomers - where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, E, m, n, o and p  
have the same meanings as defined in claim 1.

20 6.) Compounds of general formula IE and their salts and optically active isomers  
- where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, E, m, n, o and p have the  
same meanings as defined in claim 1.

7.) Compounds of general formula IF and their optically active isomers - where  
25 Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, o and p have the same meanings as  
defined in claim 1.

8.) Compounds according to claim 1.

1-naphthylmethyl 2-butyryl ether,  
30 2-propynyl-1,3-benzodioxol-5-carboxylate,  
1-[(2-butyryloxy)-ethyl]-3,4-dimethoxybenzene.

2,6-dichloro-1-(2-butynyloxy-methyl)benzene,

1-[1-(2-butynyloxy) propyl]naphthalene,

R-(+)-2-[1-(2-butynyloxy) ethyl]naphthalene,

5-[ (but-2-ynyloxy)methyl]-1,3-benzodioxole,

5 5-[2-methyl-1-(2-butynyloxy)propyl]-1,3-benzodioxole,

5-[ (but-2-ynyloxy)phenylmethyl]-1,3-benzodioxole

2-[(2-butynyloxy) methyl]-1,4-benzodioxane,

2,3-dihydro-2,2-dimethyl-7-(3-pentyloxy)benzofurane.

- 10 9.) Process for the preparation of compounds of general formula I, where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, X, Y, E, m, n, o, and p, have the same meanings as defined in claim 1.

characterized by, that

- 15 a.) for the preparation of compounds of general formula IA, where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meanings as defined in claim 1.,

compounds of general formula II and III are reacted. where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meanings as defined in claim 1.,

- 20 A and B are groups suitable to form ester bond,

b.) to prepare compounds of general formula IB, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, Y, E, m, o, and p, have the same meanings as defined in claim 1.,

compounds of general formula IV and V are reacted. where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>,

- 25 R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meanings as defined in claim 1., and C and D are groups suitable to form amide bond.

c.) to prepare compounds of general formula IC, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meanings as defined in claim 1., R<sup>3</sup>

- 30 and R<sup>4</sup> independently mean H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl,

compounds of general formula VI and VII are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p have the same meanings as defined in claim 1.. R<sup>3</sup> and R<sup>4</sup> independently mean H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl. F and G are groups suitable to form ether bond.

5

d.) to prepare compounds of general formula ID, wherein Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>2</sup>R<sup>4</sup>)<sub>n</sub>-N- stands for a carboximide group. R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, o, and p, have the same meanings as defined in claim 1..

the carboximide of general formula VIII is reacted with the compound of general formula IX, wherein R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, o, and p, have the same meanings as defined in claim 1. and Lg represents a leaving group,

10

e.) to prepare compounds of general formula IE, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, E, m, n, o, and p, have the same meanings as defined in claim 1.,

15

compounds of general formula X and XI are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meanings as defined in claim 1., H and I represent groups, suitable to form a -N-

20

R<sup>10</sup> group where the meaning of R<sup>10</sup> is the same as defined in claim 1..

f.) to prepare compounds of general formula IF, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, o, and p, have the same meanings as defined in claim 1..

25

compounds of general formula XII and IX are reacted, where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, n, o, and p, have the same meanings as defined in claim 1.. and Lg represents a leaving group, and

30

if desired, the compound of general formula I thus obtained is transformed into its salts, or liberated from its salts, and, if desired, the optically active isomers are separated.

10.) Pesticide composition comprising as active ingredient 0.0001-99.9 % by mass of a compound of the general formula I,

where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, m, n, o and p have the

5 same meanings as defined in claim 1.,

and optionally other pesticide active ingredient(s), beside carriers and other auxiliary materials.

11.) Arthropodicide composition comprising as active ingredient 0.0001-99.9 % by mass of a compound of the general formula I,

10 where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, m, n, o and p have the same meanings as defined in claim 1.,

and optionally other arthropodicide active ingredient(s), beside carriers and other auxiliary materials.

15

12.) Composition according to claim 11, characterized by, that it contains as other active ingredient

Acetamide derivatives: e.g. oxamyl;

Benzoylurea compounds: e.g. flucycloxuron, hexaflumuron, teflubenzuron,  
20 triflumuron;

Benzoylurea like IGR compounds;

Bicycloheptadien compounds: e.g. heptenophos;

Cross-bridged diphenyl compounds: e.g. etofenprox, bromopropylate, methoxychlor, temephos, tetradifon;

25 Carbamates: e.g. aminocarb, aldicarb, aldoxycarb, asulam, bendiocarb, benfuracarb, carbaryl, carbetamide, carbofuran, carbosulfan, diethofencarb, dioxacarb, ethiofencarb, fenobucarb, fenoxycarb, furathiocarb, isoprocarb, methomyl, oxamyl, pirimicarb (pirimor), propoxur, thiodicarb, thiofanox, xylylcarb;

30 Carbamoyloxime derivatives: e.g. alanycarb, butocarboxim;

Cyclodienes: e.g. aldrin, chlordane, endosulfan, heptachlor;

- Diazoles: fipronil;  
Hydrazides: RH 5992, RH 5849, CGA 215'944;  
Nereistoxin analogues: pl. bensultap;  
Nitroimidazolidinylenamines: e.g. imidacloprid;  
5 Organophosphor compounds e.g. quinalphos, diazinon, phosalone, dimethoate, azinphos-methyl,  
Organotin compounds e.g. azocyclotin, cyhexatin, fenbutatin oxide SSI-121;  
Phenoxy compounds: e.g. diafenthiuron;  
Pyrroles: e.g. pyrazophos;  
10 Pyrethroides: e.g. allethrin, bioallethrin (esbol), acrinathrin, fenvalerate, empenethrin, prallethrin, resmethrin, MTI-800, flufenprox, permethrin, tetramethrin, cypermethrin and their isomers and isomer-combinations;  
Pyridazinones: e.g. pyridaben;  
Pyridine derivatives: e.g. chlorpyrifos;  
15 Pyrimidine derivatives: e.g. pyrimiphos-ethyl, pyrimiphos-methyl;  
Pyrroles: e.g. AC 303-t, 630;  
Quinazolines: e.g. fenazaquin;  
Terpenoid derivatives: e.g. methoprene;  
Tetrazines: e.g. clofentezine, SzI-121 (flufenzin);  
20 Thiadiazines: e.g. buprofezin;  
Thiazolidin: pl. hexythiazox;  
Triazoles: pl. isazophos, RH 7988;  
Chlorinated hydrocarbons: lindane;  
Macrocyclic lactones;  
25 Tebufenpyrad;  
Fenpyroximate;  
Triazamate;
- 13.) Compositions according to claims 11. and 12, comprising a s active  
30 ingredient of general formula I one or more of the following compounds:  
1-naphthylmethyl 2-butyryl ether,

- 2-propynyl-1,3-benzodioxol-5-carboxylate.  
1-[(2-butynyloxy)-ethyl]-3,4-dimethoxybenzene,  
2,6-dichloro-1-(2-butynyloxy-methyl)benzene.  
1-[1-(2-butynyloxy)propyl]naphthalene,  
5 R-(+)-2-[1-(2-butynyloxy)ethyl]naphthalene,  
5-[(but-2-ynyloxy)methyl]-1,3-benzodioxole,  
5-[2-methyl-1-(2-butynyloxy)propyl]-1,3-benzodioxole,  
5-[(but-2-ynyloxy)phenylmethyl]-1,3-benzodioxole,  
2-[(2-butynyloxy)methyl]-1,4-benzodioxane,  
10 2,3-dihydro-2,2-dimethyl-7-(3-pentyloxy)benzofuran.

- 14.) Composition according to claims 11-14 comprising as active ingredient 0.0001-99.9 % by mass of a compound of the general formula I, where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, m, n, o and p have the same meanings as  
15 defined in claim 1., and a carbamate suitable for extermination of arthropoda, preferably carbofuran.

- 15.) Composition according to claim 14 containing (2-butynyloxy-methyl)-3,4-dimethoxybenzene, as compound of the general formula I.  
20

- 16.) Composition according to claim 14 containing 5-[(but-2-ynyloxy)methyl]-1,3-benzodioxole, as compound of the general formula I.

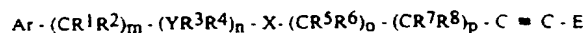
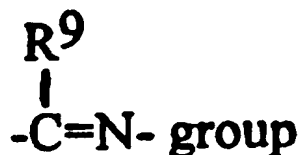
- 17.) Process for extermination of pests, preferably arthropoda, comprising  
25 treating pests, preferably arthropoda with a suitable amount of a composition of claims 10 or 11, if desired in such a way that the compositions containing compounds of the general formula I, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, m, n, o and p have the same meanings as defined in claim 1., and the compositions containing the known active ingredients are used in a tank  
30 mixture or subsequently.



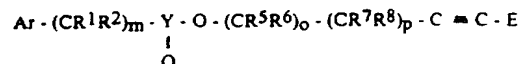
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification</b> <sup>6</sup> : <b>C07C 43/166, A01N 31/04, C07C 43/215,</b> <b>43/176, C07D 317/48, 307/79, 319/20,</b> <b>A01N 31/16, 43/30, 43/32, 43/08</b>	<b>A3</b>	<b>(11) International Publication Number:</b> <b>WO 97/19040</b>  <b>(43) International Publication Date:</b> <b>29 May 1997 (29.05.97)</b>
<b>(21) International Application Number:</b> <b>PCT/HU96/00069</b>  <b>(22) International Filing Date:</b> <b>19 November 1996 (19.11.96)</b>  <b>(30) Priority Data:</b> <b>P 95 03318</b> <b>21 November 1995 (21.11.95)</b> <b>HU</b>  <b>(71) Applicant (for all designated States except US):</b> <b>CHINOIN</b> <b>GYÓGYSZER ÉS VEGYÉSZETI TERMÉKEK GYÁRA</b> <b>RT. [HU/HU]; Tó u. 1-5, H-1045 Budapest (HU).</b>  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> <b>ARVAI, Géza [HU/HU];</b> <b>Róbert K. krt. 20, H-1138 Budapest (HU). BAKONYVÁRI,</b> <b>Ildikó [HU/HU]; Damjanich u. 4/a, H-8200 Veszprém</b> <b>(HU). BERTÓK, Béla [HU/HU]; Rizling u. 16, H-1223</b> <b>Budapest (HU). CSÍZ, László [HU/HU]; Tulipán u. 5, H-</b> <b>2030 Érd (HU). CZUDOR, Irén [HU/HU]; Kiránduló u. 1/a,</b> <b>H-1222 Budapest (HU). KURUCZNÉ, R., Zsuzsa [HU/HU];</b> <b>Emőke u. 1/b, H-2030 Érd (HU). PAP, László [HU/HU];</b> <b>Gyöngyvirág u. 23, H-2030 Érd (HU). SZÉKELY, István</b> <b>[HU/HU]; Krajcár u. 6, H-2110 Dunakeszi (HU).</b>  <b>(74) Common Representative:</b> <b>CHINOIN GYÓGYSZER ÉS</b> <b>VEGYÉSZETI TERMÉKEK GYÁRA RT; Iparjogi</b> <b>Osztály, Tó u. 1-5, H-1045 Budapest (HU).</b>	<b>(81) Designated States:</b> <b>AL, AM, AT, AU, AZ, BA, BB, BG, BR,</b> <b>BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE,</b> <b>HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS,</b> <b>LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL,</b> <b>PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA,</b> <b>UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ,</b> <b>UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ,</b> <b>TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR,</b> <b>GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF,</b> <b>BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</b>  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>  <b>(88) Date of publication of the international search report:</b> <b>3 July 1997 (03.07.97)</b>	

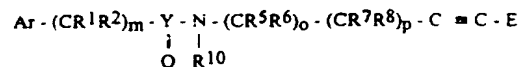
**(54) Title:** PESTICIDE COMPOUNDS, COMPOSITIONS AND PROCESS FOR THE PREPARATION THEREOF



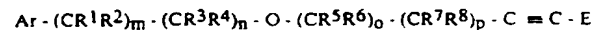
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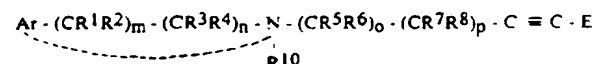
1A



1B



1C



1D

**(57) Abstract**

The invention relates to compounds of general formula (1), their optically active isomers and salts wherein Ar = alicyclic, aromatic or one or more heteroatom containing heterocyclic moiety, optionally substituted by one or more alkoxy-, methylenedioxy-, alkyl-, halogen-, haloalkyl-, or nitro-group and/or condensed with a benzene ring; R<sup>1</sup>, R<sup>2</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, R<sup>3</sup>, R<sup>4</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, or R<sup>3</sup>, R<sup>4</sup> are together =O, Y = C; PO, or YR<sup>3</sup>R<sup>4</sup> together (a) group; X = -O-; -NR<sup>10</sup>-, R<sup>9</sup> = H, alkyl, phenyl, substituted phenyl; R<sup>10</sup> = H, alkyl; R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> are independently H, alkyl, alkenyl, haloalkyl, or Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(YR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X- form together a carboximide group; E = H, halogen, methyl; m = 0, 1, 2; n = 0, 1; o = 0, 1, 2; p = 0, 1, 2, with the proviso, that the sum of the atoms or groups of the -(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X-(CR<sup>5</sup>R<sup>6</sup>)<sub>o</sub>-(CR<sup>7</sup>R<sup>8</sup>)<sub>p</sub> bridge skeleton is 3 and the -C=C-E skeleton forms with the atoms of the bridge a linear chain, consisting of 6 atoms ending preferably in a methyl group, furthermore with the proviso, that if Ar stands for a naphthyl group, Y means C-atom, X means O-atom, R<sup>3</sup> and R<sup>4</sup> together cannot mean =O. The compounds of general formula (1) according to the invention can be applied as active ingredients of pesticide, preferably arthropodicide compositions, and as synergists of other arthropodicide active ingredients.

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## INTERNATIONAL SEARCH REPORT

International Application No.  
HU 96/00069

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C43/166 A01N31/04 C07C43/215 C07C43/176 C07D317/48  
C07D307/79 C07D319/20 A01N31/16 A01N43/30 A01N43/32  
A01N43/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, vol. 16, no. 5, 1968, WASHINGTON US, pages 779-786, XP002029949 R. M. SACHER ET AL: "Propynyl naphthyl ethers as selective carbamate synergists" cited in the application see Table I, compound no. XIII and Fig. 1 ---	1,4, 9-12,17
X	US 3 954 793 A (D. J. HENNESSY) 4 May 1976  see column 2, line 32 - column 4, line 55; examples 1,2,5,6 & DE 22 35 005 A cited in the application --- -/--	1,4,7, 9-12,14, 17

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

Initial Application No.

PCT/HU 96/00069

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 718 686 A (M. S. CHODNEKAR) 27 February 1973 see column 4, line 3 - column 7, line 24; examples 44-48 ---	1,2,4, 9-11,17
X	US 3 402 179 A (K. F. MINOO-SHI) 17 September 1968 see example 1; table 1 & NL 6 600 916 A cited in the application ---	1,5, 9-12,17
A	GB 2 161 163 A (KUREHA KAGAKU KOGYO) 8 January 1986 see claims -----	1,2, 9-11,17

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
/HU 96/00069

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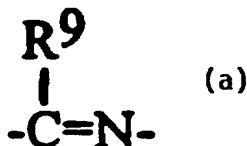
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : C07C 43/166, A01N 31/04, C07C 43/215, 43/176, C07D 317/48, 307/79, 319/20, A01N 31/16, 43/30, 43/32, 43/08	A3	(11) International Publication Number: <b>WO 97/19040</b>
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<p>(21) International Application Number: PCT/HU96/00069</p> <p>(22) International Filing Date: 19 November 1996 (19.11.96)</p> <p>(30) Priority Data: P 95 03318 21 November 1995 (21.11.95) HU</p> <p>(71) Applicant (for all designated States except US): CHINOIN GYÓGYSZER ÉS VEGYÉSZETI TERMÉKEK GYÁRA RT. [HU/HU]; Tó u. 1-5, H-1045 Budapest (HU).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): ARVAI, Géza [HU/HU]; Róbert K. krt. 20, H-1138 Budapest (HU). BAKONYVÁRI, Ildikó [HU/HU]; Damjanich u. 4/a, H-8200 Veszprém (HU). BERTÓK, Béla [HU/HU]; Rizling u. 16, H-1223 Budapest (HU). CSÍZ, László [HU/HU]; Tulipán u. 5, H- 2030 Érd (HU). CZUDOR, Irén [HU/HU]; Kiránduló u. 1/a, H-1222 Budapest (HU). KURUCZNÉ, R., Zsuzsa [HU/HU]; Emőke u. 1/b, H-2030 Érd (HU). PAP, László [HU/HU]; Gyöngyvirág u. 23, H-2030 Érd (HU). SZÉKELY, István [HU/HU]; Krajcár u. 6, H-2110 Dunakeszi (HU).</p> <p>(74) Common Representative: CHINOIN GYÓGYSZER ÉS VEGYÉSZETI TERMÉKEK GYÁRA RT; Iparjogi Osztály, Tó u. 1-5, H-1045 Budapest (HU).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> <p>(88) Date of publication of the international search report: 3 July 1997 (03.07.97)</p>

(54) Title: PESTICIDE COMPOUNDS, COMPOSITIONS AND PROCESS FOR THE PREPARATION THEREOF



## (57) Abstract

The invention relates to compounds of general formula (1), their optically active isomers and salts wherein Ar = alicyclic, aromatic or one or more heteroatom containing heterocyclic moiety, optionally substituted by one or more alkoxy-, methylenedioxy-, alkyl-, halogen-, haloalkyl-, or nitro-group and/or condensed with a benzene ring; R<sup>1</sup>, R<sup>2</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, R<sup>3</sup>, R<sup>4</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, or R<sup>3</sup>, R<sup>4</sup> are together =O, Y = C; PO, or YR<sup>3</sup>R<sup>4</sup> together (a) group; X = -O-, -NR<sup>10</sup>-, R<sup>9</sup> = H, alkyl, phenyl, substituted phenyl; R<sup>10</sup> = H, alkyl; R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> are independently H, alkyl, alkenyl, haloalkyl, or Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(YR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X- form together a carboximide group; E = H, halogen, methyl; m = 0, 1, 2; n = 0, 1; o = 0, 1, 2; p = 0, 1, 2, with the proviso, that the sum of the atoms or groups of the -(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X-(CR<sup>5</sup>R<sup>6</sup>)<sub>o</sub>-(CR<sup>7</sup>R<sup>8</sup>)<sub>p</sub> bridge skeleton is 3 and the -C≡C-E skeleton forms with the atoms of the bridge a linear chain, consisting of 6 atoms ending preferably in a methyl group, furthermore with the proviso, that if Ar stands for a naphthyl group, Y means C-atom, X means O-atom, R<sup>3</sup> and R<sup>4</sup> together cannot mean =O. The compounds of general formula (1) according to the invention can be applied as active ingredients of pesticide, preferably arthropodicide compositions, and as synergists of other arthropodicide active ingredients.

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## PESTICIDE COMPOUNDS, COMPOSITIONS AND PROCESS FOR THE PREPARATION THEREOF

This invention relates to alkynyl pesticide compounds of the general formula I., pesticide compositions containing the active ingredients of general formula I..

- 5 furthermore the pesticide synergists of general formula I., and synergized pesticide compositions with known pesticide active ingredients, and the process for the preparation thereof.

In general formula I the substituents have the following meanings:

- 10 Ar = an alicyclic-, aromatic-, or one or more heteroatom containing heterocyclic moiety, optionally substituted by one or more alkoxy, methylenedioxy, alkyl, halogen, haloalkyl or nitro group, and/or condensed with a benzene ring,  
 $R^1, R^2$  = independently hydrogen, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl,  
 15  $R^3, R^4$  = independently hydrogen, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, or  
 $R^3, R^4$  are together =O;  
 $Y = C, =PO$ , or
- 20  $YR^3R^4$  form together a  $\begin{array}{c} R^9 \\ | \\ -C=N- \end{array}$  group;  
 $X = -O-; -NR^{10}-$ ;  
 $R^9$  = hydrogen, alkyl, phenyl, substituted phenyl;  
 $R^{10}$  = hydrogen, alkyl;  
 $R^5, R^6, R^7, R^8$  are independently hydrogen, alkyl, alkenyl, haloalkyl, or
- 25 Ar-( $CR^1R^2$ )<sub>m</sub>-( $YR^3R^4$ )<sub>n</sub>-X- form together a carboximide group;  
 $E$  = hydrogen, halogen, methyl;  
 $m = 0, 1, 2$ ;  
 $n = 0, 1$ ;  
 $o = 0, 1, 2$ ;  
 30  $p = 0, 1, 2$ ,

with the proviso that the sum of the atoms or groups of the bridge  $-(CR^1R^2)_m-(CR^3R^4)_n-X-(CR^5R^6)_o-(CR^7R^8)_p$  is 3 and the  $-C=C-E$  skeleton with the  
5 atoms of the bridge forms a linear chain, consisting of 6 atoms ending favorably in a methyl group.

furthermore with the proviso that if Ar is naphthyl group. Y means C-atom. X means O-atom.  $R^3$  and  $R^4$  together can not mean  $=O$ .

The invention includes furthermore the salts and the optically active isomers of  
10 the compounds of general formula I.

Narrower groups within compounds of general formula I. are represented by the compounds of general formula IA. IB. IC. ID. IE. IF. their salts and optically active isomers, where the meanings of the substituents are the same, as defined above.

15

Favourable representatives of the compounds of general formula I. are:

1-naphthyl-methyl 2-butylnyl ether,

2-propynyl-1,3-benzodioxol-5-carboxylate,

1-[(2-butylnyloxy)-ethyl]-3,4-dimethoxybenzene.

20 2,6-dichloro-1-(2-butylnyloxymethyl)benzene.

1-[1-(2-butylnyloxy)propyl]naphthalene.

R-(+)-2-[1-(2-butylnyloxy)ethyl]naphthalene.

5-[(but-2-ynyloxy)methyl]-1,3-benzodioxole.

5-[2-methyl-1-(2-butylnyloxy)propyl]-1,3-benzodioxole.

25 5-[(but-2-ynyloxy)phenylmethyl]-1,3-benzodioxole.

2-[(2-butylnyloxy)methyl]-1,4-benzodioxane.

2,3-dihydro-2,2-dimethyl-7-(3-pentyloxy)benzofuran

In the term Ar the aromatic group is favourably phenyl or naphthyl group.

30 Ar as a heterocyclic moiety may contain one or more O, S, N heteroatoms, it may favourably represent benzodioxole-, benzodioxane-, 2-benzofuran-, 7-benzofuran-moieties.



The alicyclic group may favourably be condensed with a benzene ring, thus for instance may represent indane group, or 1,2,3,4-tetrahydronaphthyl group. The carboximide group may favourably represent phthalimide moiety.

5 The aromatic, heterocyclic and alicyclic Ar groups are optionally substituted by C<sub>1-4</sub> alkoxy-, methylenedioxy-, C<sub>1-4</sub> alkyl-, halogen-, C<sub>1-4</sub> haloalkyl- or nitro group.

Compounds which are non-toxic, or only slightly toxic alone, but given together with a pesticide, preferably arthropodicide agent they enhance markedly the  
10 potency of the latter, are called *synergists*. These materials may in principle act in several ways, however they exert their effect decisively by blocking the metabolism of the active substance. Metabolism may proceed via oxidative, hydrolytic, conjugative and absorption reactions and by the variations thereof. At present there is no unambiguous example for a synergist acting at the receptor  
15 level, neither do they play an important role in the praxis.

The synergistic potency e.g. in the case of insecticides is characterized by the so-called SR synergist ratio which is given as follows:

$$\text{SR}_{50} = \frac{\text{LD}_{50}\text{insecticide}}{\text{LD}_{50}\text{insecticide} + \text{synergist}}$$

20

The more the SR<sub>50</sub> value differs from 1, the higher is the synergistic potency. The use of synergists in arthropodicidal preparations is very attractive, since they afford a possibility to come out with new preparations with practically all  
25 representatives of the area. These new preparations, compared to the previous ones, promise to be less expensive, less toxic, more selective, encountering less environmental hazard, suppressing the evolution of resistance, and being active also on strains which already evolved resistance.

Following the discovery of synergists and the reveal of their mode of action, a  
30 wide-range research and development work started from the mid 60-ies till the late 70-ies to work out new synergists. This research, however resulted only a

few molecules which really attained application (at present the number of the registered insecticide synergists is less than 10). These compounds are of basic scientific importance in the research of resistance (K. F. Raffa and T. M. Priester, *J. Agric. Entomol.*, 2(1), 27-45, (1985)), however, there are only 2-3  
5 molecules listed as products in the Pesticide Manual, and only two materials (PBO, MGK264) which are actually on the market. The field application has been restricted by several factors: it is not easy to find a chemical tool which can be used selectively and safely, and the cost/effectiveness ratio of which is competitive with that of the active ingredient. To apply a synergist  
10 economically, it must be highly potent, it must act at small doses (not exceeding the original dose of the active ingredient).

On the basis of their chemical structures the presently known arthropodicide synergistic compounds may be divided into the following groups:

### 1.3-methylenedioxyphenyl (MDP) derivatives

15 ### O-2-propynyl and propynyl-homologues and their derivatives (ethers, oxim-ethers, esters)

### N-alkyl derivatives

### phosphor esters

### other derivatives e.g. thiocyanates, polyhalo ethers etc.

20 The compounds may also be divided into groups on the basis of their target of attack [K. F. Raffa and T. M. Priester, *J. Agric. Entomol.*, 2(1), 27-45, (1985)], but this grouping is rather theoretical, less exact, first of all because the actual metabolic processes are not fully known. The metabolism of most of the compounds proceeds consecutively, but may also proceed simultaneously, and  
25 may follow several mechanisms, thus the division is less informative, even if we consider the first step of the cascade degradation as the decisive step.

For the metabolic degradation of most arthropodicides first of all the oxygenase system is responsible. It is agreed in the literature that the compounds of this  
30 group exert their activity basically by blocking the cytochrome P-450 enzyme of the microsomal oxidation system [John E. Cassida, *J. Agr. Food Chem.*, 18(5),

- 753-772. (1970). R. M. Sacher, R. L. Metcalf and T. R. Fukuto; *J. Agr. Food Chem.*, **16**(5), 779-786. (1968)]. The enzymes forming the structurally analogous group of so-called isoenzymes constitute the major part of the detoxification system of the organisms [Ortiz de Montellano, P. R., Ed.
- 5 *Cytochrome P-450: Structure Mech. and Biochem.*, Plenum New York, (1986)]. They perform detoxification via mono-oxygenation of the substrate, producing a more polar product, which possibly after further transformations can be eliminated by the organism. The system degrades very different structures by the same way. Therefore they are also designated as Mixed Function Oxygenases
- 10 (MFO) and Polysubstrate Monooxygenases (PSMO).

On that basis one could expect that the surface of the enzyme is aspecific for the synergist, too. Quite the contrary, we have found that the compounds may be optimized.

- 15 For the isolation and testing of the Cytochrome P-450 enzymes of insects there are standard methods available [J. G. Scott and S. S. T. Lee; *Arch. Insect Biochem. and Phys.*, **24**, 1-19, (1993)]. The enzymes of various species may show great similarities, but they may also differ significantly from each other. The synergists known from the literature and investigated by us belong to the
- 20 group of O-2-propynyl, and propynyl-homologues and their derivatives (ethers, oxim-ethers, esters). As shown by the literature they exhibit different potency for the different species, which means that the oxidation capacity of the species varies to a certain extent. This is the reason for the high insect/mammal selectivity and synergist selectivity, characteristic for that group of compounds.
- 25 These selectivities, which cannot be directly explained by the above mode of action, are the bases of the development and safe application. On the other hand this is the reason why these compounds have not become commercially available. For all the compounds of the group prepared and evaluated so far we can tell, in general, that their effect was exclusively bound to the propynyl side-chain, this chain has been substituted in the allylic position by various aryl rings

mainly through an oxygen atom. The compounds known as yet may be divided into the following groups:

- #### Phenyl propargyl ethers [Fellig et. al., *J. Agr. Food Chem.*, **18**(5), 78, (1970)]
- 5 #### Benzyl propargyl ethers [Ciba Geigy, *Ger. Offen.* **2 235 005** (1972)]
- #### Benzaldoxime propargyl ethers [Ciba Geigy, *Ger. Offen.* **2 016 190** (1970)]
- #### Naphthoic acid propargyl esters [Hoffman-La Roche, *Belg. Patent.* **867 849** (1978)]
- 10 #### Alkynylphthalimides [FMC, *Ger. Patent.* **1 217 693** (1966)]
- #### Phenylphosphonic acid propargyl esters [Niagara Chem. Div., FMC Corp., Technical Data Sheet on NIA 16824, (1968)]

The first two groups are sub-divided into further groups owing to the high variability of the aromatic group and its substituents. Thus, there are known

15 naphthyl propargyl ethers [Hoffman-La Roche, *US* **3 362 871** (1968); Ciba Geigy, *Ger. Offen.* **2 100 325** (1971)],

4-hydroxyquinoline propargyl ethers [Alkaloida, *HU* **210 557**, (1992)],

methylenedioxybenzyl propargyl ethers [Sumitomo, *JP.* **03 01177**, (1973)] and

alfa-substituted methylenedioxybenzyl propargyl ethers [Sumitomo, *JP.*

20 **61 24585, 61 24586** (1986)].

In a study about naphthyl propynyl ethers it has been concluded that butynyl ethers, first of all 3-butynyl ethers are more potent than the analogous propargyl and pentynyl ethers [R. M. Sacher et. al., *J. Agr. Food Chem.*, **16**, 779-786, (1968)]. Interestingly, however there was no continuation of that work, the

25 discovery has not been patented, either. Detailed analysis of the literature data suggest, that the propynyl side-chain cannot be replaced by homologous chains, since the publications and patents relate further on to propargyl derivatives.

In order to clear this contraversion we have prepared the compounds in question, and found that in contrast to what was disclosed in the literature, the 2-

30 butynyl derivative (the one ending in a methyl group) is more potent than the 3-butynyl derivative; the alpha-isomers are more potent than the analogous beta-

isomers: and the 3-pentynyl derivative is more potent than the 2-butynyl derivative. These data suit well in our theory, and the data given in the literature might be the reason why this direction was not followed by others.

Similarly, there is a contraversion regarding the activity of the 4-

5 pentynylphthalimide derivatives: although they proved to be potent synergists of allethrin, they antagonized with pyrethrin [H. Jaffe, J. L. Neumeyer, *J. Med. Chem.*, 13, 901, (1970)]. In these structures again, the alkynyl chain ends in triple bond. The hybriide variations of these structures, namely the N-alkyloxy-O-propargyl-phthalimides have also been prepared, here again the triple bond is  
10 in terminal position [Sumitomo, *NL*, 6 600 916 (1966)].

To sum up, the most active representatives of the group, although on some tests exhibited outstanding activity, and were superior regarding their synergist/active ingredient ratio [D. J. Henessy, *Biochemical Toxicology of Insecticides*, Ed., R. D. O'Brian & I. Yamamoto, Academic Press, 105-114, (1970)], have never been  
15 applied in the praxis. This has several reasons: their activity did not reach the potency of earlier, well-established derivatives, they exhibited activity only in a narrow range, their potency was highly species-dependent, and within one species it depended greatly on the "strength" of the individual. Their safe and broad application was not therefore ensured.

20 The alkynyl compounds listed above are all derivatives of a common optimal structure, but the authors did not realize the relationships, and have not prepared the most active representatives, alloying and improving the advantages of these groups of compounds.

We have experimentally tested, compared and analysed the biological effect of  
25 the known compounds, as well as that of the new derivatives prepared by us, and revealed the structural element which is responsible for the effect. On that basis we have prepared new compounds which surpass significantly the activity of the earlier ones and combine those properties which ensure effectiveness on more species and with more known active ingredients.

30 The integral part of the present invention is the discovery, that in the optimal compounds the carrier of the activity is a triple bond of an alkynyl structure with

an electron-rich Ar ring, which is connected to the triple bond through a mobile bridge consisting of three atoms. The atoms of the bridge are variable, and may have substituents, and so is the ring. To enhance the activity it is favourable to introduce lipophilic and electron-rich atoms and substituents. Thus the atoms of the bridge may be -besides of carbon atoms- oxygen, sulphur, nitrogen, and phosphor heteroatoms. These atoms may be linked through single or multiple bonds to each other and optionally with further substituents containing the above heteroatoms they may be substituted to further functional groups or derivatives. The atoms may be replaced by each other. The first element of the bridge may with its substituent form a ring, which may be attached to the aromatic ring, and thus may be part of the electron-rich moiety. Into the ring, linked to the bridge, heteroatoms, as listed above, may also be incorporated, and the effect may be further enhanced by the introduction of alkoxy, halogen, alkyl, haloalkyl or nitro substituents. The ring may be 5-, 6-, or 7-membered and may be condensed with a further ring, which is built according to the above principles, and may incorporate the first element of the bridge. Compounds in which the acetylenic hydrogen of the alkynyl side-chain is replaced by a methyl group exhibit higher activity than the the analogues with terminal triple bond. Keeping these rules we can carry out new substitutions by which we can modify the character of the compounds, according to the demand (lipophilicity, translaminarity, systemicity, etc.) of the application area.

Of the isomers of optically active compounds, e.g.  $\alpha$ -methyl-substituted benzyl derivatives, the R(+)-enantiomers are more potent than the S(-)-enantiomers. The difference between the activities of the isomers is growing with an enhancing activity of the racemic mixture.

The compounds developed by us are new, they are characterized by outstanding mammal/insect selectivity and high potency, exerted at low dose related to the active ingredient. This is attributed to the outstanding high receptor affinity of our compounds. In comparative experiments the indices of our compounds

highly surpassed those of earlier known synergists for active ingredients, whose metabolism is based on microsomal oxidation. This high activity and selectivity were also demonstrated in field studies conducted on small plots. The compounds did not show fito-toxicity, they did not separate from the active ingredients, their physico-chemical parameters fitted well with those of the active ingredient. Through these features the dose/efficacy/cost value, which earlier hindered the application, could favourably be modified and the application became possible.

With the active substances of general formula I the effect of the following known arthropodicide active ingredients may favourably be synergized:

Acetamide derivatives: e.g. oxamyl;

Benzoylurea compounds: e.g. flucycloxuron, hexaflumuron, teflubenzuron, triflumuron;

Benzoylurea like IGR compounds;

Bicycloheptadien compounds: e.g. heptenophos;

Cross-bridged diphenyl compounds: e.g. etofenprox, bromopropylate, methoxychlor, temephos, tetradifon;

Carbamates: e.g. aminocarb, aldicarb, aldoxycarb, asulam, bendiocarb, benfuracarb, carbaryl, carbetamide, carbofuran, carbosulfan, diethofencarb, dioxacarb, ethiofencarb, fenobucarb, fenoxycarb, furathiocarb, isoprocarb, methomyl, oxamyl, pirimicarb (pirimor), propoxur, thiodicarb, thiofanox, xylylcarb;

Carbamoyloxime derivatives: e.g. alanycarb, butocarboxim;

Cyclodienes: e.g. aldrin, chlordane, endosulfan, heptachlor;

Diazoles: fipronil;

Hydrazides: RH 5992, RH 5849, CGA 215'944;

Nereistoxin analogues: pl. bensultap;

Nitroimidazolidinylenamines: e.g. imidacloprid;

Organophosphor compounds e.g. quinalphos, diazinon, phosalone, dimethoate, azinphos-methyl,

Organotin compounds e.g. azocyclotin, cyhexatin, fenbutatin oxide SSI-121;

- Phenoxy compounds: e.g. diafenthiuron;  
Pyrazoles: e.g. pyrazophos;  
Pyrethroides: e.g. allethrin, bioallethrin (esbol), acrinathrin, fenvalerate, emperthrin, prallethrin, resmethrin, MTI-800, flufenprox, permethrin,  
5 tetramethrin, cypermethrin and their isomers and isomer-combinations;  
Pyridazinones: e.g. pyridaben;  
Pyridine derivatives: e.g. chlorpyrifos;  
Pyrimidine derivatives: e.g. pyrimiphos-ethyl, pyrimiphos-methyl;  
Pyrroles: e.g. AC 303-t, 630;  
10 Quinazolines: e.g. fenazaquin;  
Terpenoid derivatives: e.g. methoprene;  
Tetrazines: e.g. clofentezine, SZI-121 (flufenzin);  
Thiadiazines: e.g. buprofezin;  
Thiazolidin: pl. hexythiazox;  
15 Triazoles: pl. isazophos, RH 7988;  
Chlorinated hydrocarbons: lindane;  
Macrocyclic lactones;  
Tebufenpyrad;  
Fenpyroximate;  
20 Triazamate:  
The above known active ingredients are described in the 8th and 10th Edition of the Pesticide Manual, European Patent Application No. 0635499 (SZI-121), A.G.Chem.New Compound review vol. 11(1993) and ACS Symposium Series 504 p. 272, respectively.  
25 Compounds of the general formula I can be most preferably used to synergize the effect of carbamates preferably carbofuran.  
We have found that the compounds have dual action, they are superior synergists of arthropodicide active ingredients, and they also hinder the individual growth of arthropoda through an effect impeding the biosynthesis of  
30 ecdison, a material, playing key role in the growth of arthropoda. There is thus an unambiguous relationship between the synergistic- and the individual



growth-hindering activities. This latter effect, beside the outstanding metabolism-blocking activity of the compounds, is also a consequence of the fact, that these materials, in contrast to the other, earlier known families of compounds, practically do not degrade, or degrade only extremely slowly in the organism of the arthropoda. Thus, when applied alone, at a long run, depending on the periods of the endocrin regulation, they are able to block the hormon synthesis and hinder the degradation of the endo and exo-biotica. Due to the toxins accumulating in the organism, the individuals become incapable of living, they do not eat, the production of eggs diminishes, and the reproduction stops.

Beside these enhanced activities, the toxicity values of the compounds on mammals did not increase. This can be attributed to the differences in the electrode potential values of microsomal oxidation systems for mammals and for arthropoda. Whereas the oxidation potential values of the higher-order organisms are high, and therefore they are able to beat the electron-barrier of the complexed synergists, the oxidation system of the arthropoda, with its small potential, is not capable to oxidate, and by this to remove the complexed molecule from the surface of the enzyme, causing the paralysis of the system. This is the reason why the compounds can be applied safely and selectively. The over-average fast degradation and excretion of the compounds from mammalia, owing to their high enzyme activity and fast enzyme binding, ensure, in contrast to the arthropoda, that these materials do not enhance the effect of biotics found or taken up by the mammalian organism, and therefore they are safe.

The effect was demonstrated by us on various arthropode species. Applied alone, or as a synergist, the compounds were active on insects, plant-louses and also on acari. In the light of the above, this fact refers again to the qualitatively different detoxification system of the mammals.

A very valuable advantage of our compounds is that on applying them to species, which already evolved resistance, the toxic dose could be reduced below the original dose of the known active ingredient (measured on susceptible strains). This has not been experienced with other synergists. This makes

possible the safe and effective management of resistant populations, complying with the modern regulations.

Beside the expected advantages mentioned above (they make possible to develop tools which are less expensive, less toxic on mammals, selective, and can suppress resistance) with the help of these compounds a number of well-established active ingredients can be renewed, the market of which has fallen back in the past years, because resistance evolved against them. (Carbofuran, Quinalphos, Cartap, Methomyl). Our compounds create new application and market possibilities, since they enhance the potency of less active materials (Resmethrin, Bioallethrin, Pirimicarb etc.) to the level of the most active compounds, without increasing their toxicity. PBO, which is on the market in big lots, but -with natural resources running low- at increasing price, and which is drawing back because of its suspected tumor provoking effect, may also be replaced with the help of our compounds.

15

The preparation of the compounds of general formula I varies depending on the different groups of compounds, and can be carried out by the chemical methods, characteristic for the preparation of these groups.

Thus

20 a.) for the preparation of compounds of general formula IA, where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meaning as defined above, compounds of general formula II and III are reacted wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meaning as defined above, A and B are groups, suitable to form ester bond.

25

b.) for the preparation of compounds of general formula IB, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, Y, E, m, o, and p, have the same meaning as defined above.

compounds of general formula IV and V are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meaning as defined above, and C and D stand for groups, suitable to form amide bond.

30

- c.) for the preparation of compounds of general formula IC, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meaning as defined above. R<sup>3</sup> and R<sup>4</sup> independently mean H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl.
- 5 compounds of general formula VI and VII are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meaning as defined above. R<sup>3</sup> and R<sup>4</sup> may independently mean H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, F and G stand for groups, suitable to form ether bond,
- 10 d.) for the preparation of compounds of general formula ID, wherein Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>2</sup>R<sup>4</sup>)<sub>n</sub>-N- stands for caboximide group, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, o, and p, have the same meaning as defined above,  
the carboximide of general formula VIII is reacted with the compounds of general formula IX, wherein R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, o, and p, have the same  
15 meaning as defined above and Lg stands for a leaving group,
- e.) for the preparation of compounds of general formula IE, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, E, m, n, o, and p, have the same meaning as defined above,
- 20 compounds of general formula X and XI are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meaning as defined above.  
H and I stand for a group, suitable to form a
- $$\begin{array}{c} \text{-N-} \\ | \\ \text{R}^{10} \end{array}$$
- 25 group, wherein R<sup>10</sup>, has the same meaning as defined above,
- f.) for the preparation of compounds of general formula IF, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, o, and p, have the same meaning as defined above,  
compounds of general formula XII and IX are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>,  
30 R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, n, o, and p, have the same meaning as defined above,  
and Lg stands for a leaving group, and

if desired, the compound of general formula I can be transformed into its salts, or may be liberated from its salts and, if desired, the optically active isomers can be separated.

5

To prepare the compounds of general formula I advantageously:

- a.) The acyl halide of general formula II is reacted with the alkynol of general formula III, or the carboxylic acid of general formula II is reacted with the alkynyl halogenide of general formula III, in the presence of an acid binding agent, or
- 10 the carboxylic acid of general formula II is reacted with the alkynol of general formula III in the presence of an activator, preferably diethyl azodicarboxylate and triphenylphosphine or dicyclohexylcarbodiimide and an acidic catalyst,
- 15 b.) The acyl halide of general formula II is reacted with the primary or secondary alkynylamine of general formula V, or the carboxamide of general formula IV is reacted with the alkynyl halogenide of general formula V, optionally in the presence of an acid-binding agent.
- 20 c.) The alcohol of general formula VI is reacted with the alkynyl halogenide of general formula VII, or the halogenide of general formula VI is reacted with the alkynol of general formula VII in the presence of a base, or the alcohol of general formula VI and the alkynol of general formula VII are reacted in the presence of an activator, preferably diethyl azodicarboxylate and
- 25 triphenylphosphine or dicyclohexylcarbodiimide and an acidic catalyst.
- d.) The carboximide of general formula VIII is reacted in the presence of a base with the alkynyl halogenide or -mesylate, -tosylate, -trifluoroacetate of general formula IX, or

30

e.) The secondary amine of general formula X is reacted with the alkynyl halogenide of general formula XI. or the halogenide of general formula X is reacted with the secondary amine of general formula XI in the presence of a base. or

5

f.) The aldoxime or ketoxime of general formula XII is reacted in the presence of a base with the alkynyl halogenide or -mesylate, -tosylate, -trifluoroacetate of general formula IX.

10 The compounds prepared and claimed by us are new, they are not disclosed in the literature. Their structures have been elucidated after purification, purity was checked by TLC and GC methods. The molecular formula of the compounds was proven by elementary analysis, and the structures were unequivocally supported by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR measurements.

15

The materials can be formulated as independent compositions or in admixture with other known arthropodicide active ingredients, and according to the application goal known carriers and other auxiliary materials may be used. Thus, by methods known per se, emulsion concentrates, microemulsions, dusters,

20 aerosols, vaporators and smokers may be prepared. [Rhone Poulenc-Geronazzo: Surfactant and Specialities for Plant Protection, Application Manual (1994), ICI: Surfactants, Application Manual (1992)].

In the course of the application the preparation containing the compound of  
25 general formula I and the preparation containing the known active ingredients(s) can be used one after the other or by making a tank-mixture of them.

To demonstrate the scope of our invention we present the following examples, without limiting the scope to the examples.

30

Examples for preparation:

Purity of the compounds was checked by TLC and GC methods: (CP 9000, CP-SIL-5CB, 60 m x 0.53  $\mu$ m, 5 ml/min  $N_2$ , FID, 220°C). As shown by these  
5 methods all compounds had purity over 95%. Structure of the materials was supported by IR,  $^1H$  and  $^{13}C$ -NMR measurements. molecular formulae were proven by elementary analysis.

## 1. Alkynyl esters

10

## General procedure

## A.)

The appropriate alkynyl alcohole was dissolved in dry benzene, pyridine was  
15 added and the mixture was cooled to 0-5°C. To this mixture the acyl chloride was added at a rate that the inner temperature does not exceed 5°C. The reaction mixture was stirred at room temperature overnight, the precipitated pyridinium hydrochloride was filtered off. The filtrate was neutralized with hydrogen chloride solution, then washed subsequently with water and saturated sodium  
20 chloride solution, dried on  $MgSO_4$  and evaporated. The raw material was purified by chromatography.

## B.)

6 mmol of the acide were dissolved in 20 ml of dry THF and 1.0 g (6 mmol) of diethyl azodicarboxylate (DEAD) were added. The mixture was cooled on an  
25 ice-water bath, and the solution of 10 mmol of the alkynol and 1.6 g (6 mmol) of triphenylphosphine in 10 ml of THF was added. The characteristic orange colour of the DEAD gradually disappeared. The solution was stirred at room temperature overnight, then it was diluted with 50 ml of ethylacetate, washed with saturated sodium chloride solution, dried and evaporated. From the residue

the triphenylphosphine oxide crystallized on addition of hexane-ethylacetate mixture. The filtrate was purified by coloumn chromatography.

	Compound	Mp(C°)	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
1.1 501	2-Propynyl 1,3-benzodioxol-5-carboxylate	69-70	3270, 3010, 2922, 2853, 2124, 1726, 1625, 1606, 1501, 1445, 1373, 1279, 1263, 1157, 1103, 1076, 1039, 762.	2.51 (1H, t, J=2.4 Hz, $\equiv$ C-H), 4.88 (2H, d, J=2.4 Hz, OCH <sub>2</sub> -C $\equiv$ ), 6.03 (2H, s, OCH <sub>2</sub> O), 6.83 (1H, d, J=8.2 Hz), 7.47 (1H, d, J=1.6 Hz), 7.66 (1H, dd, J=8.2, 1.6 Hz)	52.34 (OCH <sub>2</sub> -C $\equiv$ ), 74.92 ( $\equiv$ CH), 77.81 (OCH <sub>2</sub> -C $\equiv$ ), 101.85 (OCH <sub>2</sub> O), 107.99, 109.59 (C-4, C-7), 123.29 (C-5), 125.71 (C-6), 147.74 (C-3a), 151.91 (C-7a), 165.07 (CO ester)
1.2 502	2-Butynyl 1,3-benzodioxol-5-carboxylate	63-64	3016, 2959, 2920, 2244, 1714, 1626, 1606, 1508, 1450, 1372, 1276, 1240, 1163, 1117, 1078, 1036, 970, 925, 758.	1.86 (3H, t, J=2.3 Hz, $\equiv$ C-CH <sub>3</sub> ), 4.84 (2H, q, J=2.3 Hz, OCH <sub>2</sub> -C $\equiv$ ), 6.03 (2H, s, OCH <sub>2</sub> O), 6.83 (1H, d, J=8.2 Hz), 7.47 (1H, d, J=1.6 Hz), 7.67 (1H, dd, J=8.2, 1.6 Hz).	3.65 ( $\equiv$ C-CH <sub>3</sub> ), 53.19 (OCH <sub>2</sub> -C $\equiv$ ), 73.33 (OCH <sub>2</sub> -C $\equiv$ ), 83.17 ( $\equiv$ C-CH <sub>3</sub> ), 101.81 (OCH <sub>2</sub> O), 107.95, 109.62 (C-4, C-7), 123.69 (C-5), 125.62 (C-6), 147.72 (C-3a), 151.78 (C-7a), 165.33 (CO ester)

## 2. Alkynyl-amides

## General procedure

The solution of the acyl chloride was reacted with the solution of the alkynylamine, in the presence of pyridine, at room temperature. The suspension was diluted washed consecutively with water, diluted hydrochloric acid solution and sodium hydrocarbonate solution, dried, evaporated and purified by chromatography and crystallisation.

	Compound	Mp(C°)	IR v(cm <sup>-1</sup> )	<sup>1</sup> H-NMR δ (ppm)	<sup>13</sup> C-NMR δ (ppm)
2.1 523	N-(2-butyryl) 3,4-methylene- dioxy- benzamide	143-144	3334, 3075, 2918, 1641, 1620, 1605, 1546, 1500, 1485, 1313, 1264, 1239, 1042.	1.82 (3H, t, J=2.4 Hz, CH <sub>3</sub> -C≡), 4.16 (2H, m, NH-CH <sub>2</sub> -C≡), 6.02 (2H, s, (CH <sub>2</sub> O) <sub>2</sub> ), 6.23 (NH), 6.81 (1H, dd, J=0.6, 7.8 Hz, H-4), 7.28-7.34 (2H, m, H-6, H-7)	3.54 (CH <sub>3</sub> -C≡), 30.37 (NH-CH <sub>2</sub> -C≡), 74.72 and 79.77 (C≡C), 101.73 (OCH <sub>2</sub> O), 107.72, 108.02 (C-4, C-7), 121.70 (C-6), 128.26 (C- 5), 148.01 (C-3a), 150.49 (C-7a), 166.37 (CONH)
2.2 535	N-(2-Butyryl)- 2-naphthamide	133-134	3295 (NH), 3055, 2922, 2913, 2850, 1641, 1629, 1602, 1541, 1414, 1309, 776, 756	1.08 (3H, t, J=2.1 Hz, CH <sub>3</sub> -C≡), 3.38 (1H, s, NH), 4.10 (2H, m, CH <sub>2</sub> - C≡), 7.60 (2H, m), 8.0 (3H, m), 8.49 (1H, s, H- 1), 9.03 (1H, t, J=5.3 Hz)	3.27 (CH <sub>3</sub> -C≡), 29.11 (- CH <sub>2</sub> -C≡), 76.77 and 78.07 (C≡C), 124.29 (C- 3), 126.90, 127.82 (three signals overlapping), 128.08, 129.07, 131.51 (C-4a), 132.32 (C-2), 134.37 (C-8a), 166.07 (CO)



5	2.3 541	N-(2-Propynyl)- l-naphthamide	105-106	3229 (NH), 3046, 2963, 2927, 2118, , 1635, 1618, 1590, 1576, 1531, 1415, 1301, 1245, 1033, 788, 773, 759, 519	2.27 (3H, t, J=2.4 Hz, H- C≡), 4.24 (2H, q, J=2.4, CH <sub>2</sub> -C≡), 6.52 (1H, broad s, NH), 7.35 (1H, t, J=8.1 Hz), 7.50 (3H, m), 7.84 (2H, m), 8.26 (1H, m)	29.62 (-CH <sub>2</sub> -C≡), 71.80 (H-C≡C), 79.43 (H- C≡C), 124.59, 125.19, 125.29, 126.41, 127.14, 128.28, 130.06 (C-8a), 130.85 (C-2), 133.34 (C- 1), 133.59 (C-4a), 169.14 (CO)
10	2.4 542	N-(2-Butynyl)- l-naphthamide	120-122	3276 (NH), 3046, 3011, 2917, 2856, 1632, 1618, 1591, 1577, 1522, 1444, 1432, 1287, 1258, 783	1.83 (3H, t, J=2.1 Hz, CH <sub>3</sub> -C≡), 4.25 (2H, q, J=2.1 Hz, CH <sub>2</sub> -C≡), 6.25 (1H, s, NH), 7.31- 7.60 (3H, m), 7.85 (2H, m), 8.32 (1H, m)	3.50 (CH <sub>3</sub> -C≡), 30.24 (- CH <sub>2</sub> -C≡), 74.47 and 79.81 (C≡C), 124.59, 125.19, 124.62, 125.09, 125.37, 126.39, 127.10, 128.26, 130.11 (C-8a), 130.75 (C-2), 133.64 and 133.75 (C-1, C-4a), 169.03 (CO)
15						
20						

## 3. Alkynylimides

## General procedure

To the solution of phthalimide in dry DMF 1 molar equivalent of dry potassium carbonate was added and to this suspension was added dropwise the toluene solution of 1 molar equivalent of alkynyl bromide. The suspension was stirred at 80 °C for 3 hours, then it was poured on ice-water. the crystals were collected and crystallized from 96% ethanol.

	Compound	Mp(C°)	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
3.1 537	N-(But-2-ynyl)- phthalimide	216-218	3090, 3040 (H-C aromatic), 2957, 2920 (CH aliphatic), 2234 (C≡C) 1768, 1718 (CO), 1609 (C=C aromatic), 1468, 1431, 1397, 1354, 1333, 1126, 1090, 952, 775, 732, 712, 629, 560, 532.	1.76 (3H, t, J=2.3 Hz, CH <sub>3</sub> -C≡), 4.32 (2H, q, J=2.3 Hz, N-CH <sub>2</sub> -C≡), 7.86-7.91 (4H, m, aromatic)	3.12 (CH <sub>3</sub> -C≡), 27.16 (N-CH <sub>2</sub> -C≡), 73.82 (CH <sub>3</sub> -C≡), 79.06 (CH <sub>2</sub> - C≡), 123.48 (C-3, C-6), 131.64 (C-1, C-2), 134.87 (C-4, C-5), 167.01 (CO)

## 4. (Aryl-alkyl)-, alkyl-alkynyl ethers

## 4.0 Preparation of 1-[(2-butynyloxy)-ethyl]-3,4-dimethoxybenzene (compound 599)

In a 50 ml flask fitted with thermometer, magnetic stirrer, addition funnel, and connected to an inert gas system, the suspension of 30 ml of dry THF and 1.5 g (0.063 mol) of NaH (cca.90 %) was prepared. To the suspension was added dropwise, at room temperature the solution of 4.0 g (0.021 mol) of  $\alpha$ -methyl-veratryl alcohol in 21 ml of dry THF. The mixture was heated under reflux conditions for 1 hour, cooled to room temperature. 4.1 g (0.0315 mol) of 1-bromo-2-butyne were added, then the heating was continued. The reaction was followed by TLC (eluent: hexane-EtOAc 4:1). The reaction is completed in about 3-4 hours.

To the cooled thick suspension 50 ml of ether was added, the mixture was filtered on Celite, the filtrate was washed with distilled water, dried on magnesium sulfate and evaporated. The residual oil was purified by column chromatography (eluent: hexane-EtOAc 4:1,  $R_f=0.37$ ).

Yield: 2.3 g (9.8 mmol), 46.9 %.

Purity of the product was checked by GC analysis: (CP 9000, CP-SIL-5CB, 60 m x 0.53  $\mu$ m, 5 ml/min  $N_2$ , FID, 250°C)  $t_R = 12.0$  min. >99%

Proof of structure:

20 Elementary analysis: ( $C_{14}H_{17}O_3$ , 233.29):

calculated: C% 72.08, H% 7.35

found: C% 69.70, H% 7.21

IR ( $CHCl_3$ )  $\nu$   $cm^{-1}$ : 2976, 2855, 2837, 1605, 1595, 1514, 1465, 1419, 1371, 1353, 1311, 1260, 1164, 1141, 1086, 1027, 864

25  $^1H$ -NMR (200 MHz,  $CDCl_3$ )  $\delta$ :

1.46 (3H, d,  $J=6.5$  Hz,  $CH-CH_3$ ), 1.85 (3H, t,  $J=2.3$  Hz,  $\equiv C-CH_3$ ),

3.83 and 4.01 (2H, ABX<sub>3</sub>  $J_{AB}=15.0$  Hz,  $J_{AX}=J_{BX}=2.3$  Hz,  $=C-CH_2O$ ),

3.87 and 3.89 (summa 6H, s each  $OCH_3$ )

4.55 (2H, q,  $J=6.5$  Hz, Ar-CHO),

30 6.80-6.89 (3H, m, aromatic).

<sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>)δ:

3.61 (≡C-CH<sub>3</sub>), 23.76 (CH-CH<sub>3</sub>), 55.87 (OCH<sub>3</sub>), 55.96 (≡C-CH<sub>2</sub>O).

75.36 (≡C-CH<sub>2</sub>), 76.40 (Ar-CH-CH<sub>3</sub>), 81.91 (≡C-CH<sub>3</sub>), 109.06 (C-2).

110.86 (C-5), 118.94 (C-6), 135.30 (C-1), 148.52 (C-3), 149.19 (C-4).

In an analogous way as described in Example 4.0 were prepared the following compounds:

	Compound	Mp(C°)	IR v(cm <sup>-1</sup> )	<sup>1</sup> H-NMR δ (ppm)	<sup>13</sup> C-NMR δ (ppm)
4.1 279	1-naphthyl- methyl 2-butyryl ether	oil	3044, 3001, 2945, 2920, 2854, 1598, 1509, 1356, 1166, 1086, 1067	1.93 (3H, t, J=2.3 Hz, C≡C-CH <sub>3</sub> ), 4.22 (2H, q, J=2.1 Hz, O-CH <sub>2</sub> -C≡C), 5.06 (2H, s, C <sub>10</sub> H <sub>7</sub> - CH <sub>2</sub> -O), 7.45 (1H, t, J=8 Hz), 7.53 (3H, m), 7.84 (1H, d, J=8.1 Hz), 7.88 (3H, m), 7.88 (1H, d, J=7.7 Hz), 8.19 (1H, d, J=8.2 Hz)	3.6 (C≡C-CH <sub>3</sub> ), 57.71 (O-CH <sub>2</sub> -C≡C), 69.72 C <sub>10</sub> H <sub>7</sub> -CH <sub>2</sub> -O), 75.10 (O-CH <sub>2</sub> -C≡C), 82.76 (O-CH <sub>2</sub> -C≡C), 124.03, 125.10, 125.72, 126.19, 126.85, 128.43, 128.72, 131.79 (C-8a), 133.06, 133.70
4.2 292	1-[1-(2- butynyloxy)- ethyl]- naphthalene	oil	3052, 2977, 2921, 2856, 1596, 1509, 1444, 1371, 1095, 1078	1.67 (3H, d, J= 6.5 Hz, CH <sub>3</sub> -CH), 1.87 (3H, t, J=2.3 Hz, ≡C-CH <sub>3</sub> ), 2.96 and 4.15 ( summa 2H, ABX, J <sub>AB</sub> =15.0 Hz, J <sub>AX</sub> =J <sub>BX</sub> =2.3 Hz, OCH <sub>2</sub> -C≡C), 5.40 (1H, q, J=6.5 Hz, C <sub>10</sub> H <sub>7</sub> - CH-O), 7.51 (3H, m), 7.61 (1H, d, J=6.8 Hz), 7.79 (1H, d, J=8.1 Hz), 7.89 (1H, dd, J=7.9, 1.8 Hz), 8.22 (1H, d, J=8.1 Hz)	3.64 (C≡C-CH <sub>3</sub> ), 22.96 (CH <sub>3</sub> -CH), 56.37 (O- CH <sub>2</sub> -C≡C), 74.29 (CH <sub>3</sub> - CH), 75.36 and 82.14 (C≡C), 123.26 (C-8), 123.52, 125.50, 125.85, 127.92, 128.83, 130.78 (C-8a), 133.88 (C-4a), 138.42 (C-1)

4.3 454	1-[1-(2-butynyloxy)-propyl]-naphthalene	oil	3058, 3048, 3000, 2962, 2932, 2923, 2876, 2856, 1598, 1509, 1460, 1105, 1062.	1.02 (3H, t, $J = 7.4$ Hz, $\text{CH}_3\text{-CH}_2$ ), 1.89 (3H, t, $J = 2.3$ Hz, $\text{C}\equiv\text{C-CH}_3$ ), 2.03 (2H, m, $\text{CH}_3\text{-CH}_2$ ), 3.95 and 4.17 (summa 2H, ABX, $J_{AB} = 15.0$ Hz, $J_{AX} = J_{BX} = 2.3$ Hz, $\text{OCH}_2\text{-C}\equiv\text{C}$ ), 5.15 (1H, t, $J = 6.4$ Hz, $\text{C}_{10}\text{H}_7\text{-CH-O}$ ), 7.53 (3H, m), 7.59 (1H, d), 7.81 (1H, d), 7.89 (3H, m), 8.27 (1H, d)	3.59 ( $\text{C}\equiv\text{C-CH}_3$ ), 10.62 ( $\text{CH}_3\text{-CH}_2$ ), 30.27 ( $\text{CH}_3\text{-CH}_2$ ), 56.54 ( $\text{O-CH}_2\text{-C}\equiv\text{C}$ ), 75.50 ( $\text{O-CH}_2\text{-C}\equiv\text{C}$ ), 80.08 and 81.96 ( $\text{OCH-naphthyl}$ and $\text{O-CH}_2\text{-C}\equiv\text{C}$ ), 123.43 (C-8), 124.40, 125.31, 125.36, 125.73, 127.91, 128.79, 131.19 (C-8a), 133.88 (C-4a), 137.12 (C-1)
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	Compound	Mp(C°)	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
4.4 472	1-[2-methyl-1-(2-butynyloxy)-propyl]-naphthalene	oil	3051, 2959, 2922, 2871, 1598, 1509, 1466, 1064.	0.87 and 1.16 (summa 6H, d each, $J = 6$ Hz, $\text{CH}(\text{CH}_3)_2$ ), 1.88 (3H, t, $J = 2.3$ Hz, $\text{C}\equiv\text{C-CH}_3$ ), 2.31 (1H, m, $\text{CH}(\text{CH}_3)_2$ ), 3.89 and 4.14 (2H summa ABX <sub>3</sub> , $J_{AB} = 15$ Hz, $J_{AX} = J_{BX} = 2.3$ Hz, $\text{OCH}_2$ ), 4.92 (1H, d, $J = 6$ Hz, $\text{CH-O}$ ), 7.53 (4H, m), 7.83 (1H, d, $J = 8$ Hz), 7.91 (1H, dd, $J = 7, 2$ Hz), 8.30 (1H, d, $J = 7.6$ Hz)	3.57 ( $\text{C}\equiv\text{C-CH}_3$ ), 19.87 and 18.77 ( $\text{CH}(\text{CH}_3)_2$ ), 34.20 ( $\text{CH}(\text{CH}_3)_2$ ), 56.71 ( $\text{OCH}_2$ ), 75.67 ( $\text{C}\equiv\text{C-CH}_3$ ), 81.77 ( $\text{C}\equiv\text{C-CH}_3$ ), 123.84 (C-8), 125.15, 125.31, 125.39, 125.60, 127.91 (C-4), 128.76 (C-5), 131.74 (C-8a), 133.87 (C-4a), 136.56 (C-1).

4.5 389	1-[(1-methyl-(2-propynyloxy)-methyl)-naphthalene]	oil	3306, 3049, 2990, 2935, 2866, 1599, 1510, 1447, 1374, 1327, 1099, 1064	1.51 (3H, d, J=6 Hz), CH <sub>3</sub> : 2.56 (1H, d, J=2 Hz), CH: 4.30 (H, qxd J=6.2 Hz) OCH: 4.91 and 5.34 (2H, AB, J <sub>AB</sub> = 15 Hz) OCH <sub>2</sub> : 7.46 (1H, dd, J=7.8 Hz), 7.54 (3H, m), 7.86 (2H, m), 8.18 (1H, mxd, J=6 Hz) aromatic	22.1, CH <sub>3</sub> , 64.25, OCH: 68.99, CH: 73.34, aryl-CH <sub>2</sub> : 83.71, CH-C: 124.11, C-8: 125.17, C-2: 125.74, C-3: 126.18, C-6: 126.92, C-7: 128.47, C-4: 128.75, C-5: 131.88, C-8a: 133.20, C-4a: 133.77, C-1
4.6 256	2-[1-(2-propynyloxy)-ethyl]-naphthalene	oil	3307, 3000, 2979, 2929, 2857, 1603, 1505, 1442, 1373, 1311, 1270, 1215, 1087, 1055, 860, 821, 633	1.58 (3H, d, J= 6.5 Hz, CH <sub>3</sub> -CH), 2.44 (1H, t, J=2.4 Hz) CH, 3.92 (1H, dd, J=2.4, 15.7 Hz) OCH <sub>a</sub> -C≡C, 4.13 (1H, dd, J=2.4, 15.7 Hz), OCH <sub>b</sub> -C≡C, 4.84 (1H, q, J=6.5 Hz, C <sub>10</sub> H <sub>7</sub> -CH-O), 7.50 (3H, m), 7.77 (1H, s), 7.85 (3H, m)	23.66 (CH <sub>3</sub> -CH), 55.55 (O-CH <sub>2</sub> -C≡C), 74.07 and 76.80 (CH-O, CCH), 79.98, (CCH), 124.11, (C-6), 125.60 (C-7), 125.90, 126.15, 127.68, 127.85, 128.5, 133.16, 133.21, 139.75 (C-1)
4.7 293	2-[1-(2-butyloxy)-ethyl]-naphthalene	oil	3051, 2977, 2920, 2854, 1602, 1444, 1084	1.57 (3H, d, J= 6.5 Hz, CH <sub>3</sub> -CH), 1.87 (3H, t, J=2.3 Hz, CH <sub>3</sub> -C), 3.90 and 4.08 (1-1H, ABX3, J=15, 2.3 Hz, OCH <sub>a,b</sub> -C≡C), 4.79 (1H, q, J=6.5, C <sub>10</sub> H <sub>7</sub> -CH-O), 7.49 (3H, m), 7.77 (1H, bs, H-1), 7.85 (3H, m)	3.64 (C≡C-CH <sub>3</sub> ), 23.78 (CH <sub>3</sub> -CH), 56.23 (O-CH <sub>2</sub> -C≡C), 75.28 (C≡C-CH <sub>3</sub> ), 76.72 (CH-CH <sub>3</sub> ), 82.10 (C≡C-CH <sub>3</sub> ), 124.14, (C-6), 125.42, 125.78, 126.05, 127.64, 127.80, 128.40, 133.07 (C-4), 133.19 (C-8), 140.14 (C-2)

	Compound	Mp(C°)	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
4.8 441	5-[(But-2-ynnyloxy)-methyl]-1,3-benzodioxole	oil	2997, 2946, 2921, 2888, 2376, 1609, 1503, 1491, 1445, 1251, 1099, 1070, 1042, 937, 865, 810	1.87 (3H, t, J=2.3 Hz, Me), 4.10 (2H, q, J=2.3 Hz, O-CH <sub>2</sub> -C $\equiv$ ), 4.47, (2H, s, O-CH <sub>2</sub> -Ar), 5.94 (2H, s, O-CH <sub>2</sub> -O), 6.76 (1H, d, J=8 Hz, H-7), 6.81 (1H, dd, J=8.15 Hz, H-6), 6.86 (1H, J=1.5 Hz, H-4)	3.52 (Me), 57.29 (O-CH <sub>2</sub> -C $\equiv$ ), 71.15 (O-CH <sub>2</sub> -Ar), 82.54 (CH <sub>3</sub> -C $\equiv$ ), 100.9 C-2, 107.95, 108.71 (C-4,7), 121.66 (C-6), 131.39, (C-5), 147.15, 147.66 (C3a, C-7a)
4.9 484	5-[2-Methyl-1-(2-butyloxy)-propyl]-1,3-benzodioxole	oil	2958, 2921, 2874, 1608, 1502, 1486, 1441, 1076, 1041, 940	0.63 and 0.94 (summa 6H, d each, J = 6.8 Hz, CH(CH <sub>3</sub> ) <sub>2</sub> ), 1.76 (3H, t, J = 2.3 Hz, C $\equiv$ -CH <sub>3</sub> ), 1.81 (1H, m, CH(CH <sub>3</sub> ) <sub>2</sub> ), 3.69 and 3.94 (summa 2H, ABX <sub>3</sub> , J <sub>AB</sub> =15.1 Hz, J <sub>AX</sub> = J <sub>BX</sub> = 2.3 Hz, OCH <sub>2</sub> ), 3.86 (1H, d, J = 7.8 Hz, CH-O), 5.87 (2H, AB, OCH <sub>2</sub> -O), 6.62 (1H, dd, J = 7.9, 1.6 Hz, 6-H), 6.68 (1H, d, J = 7.9 Hz, 7-H), 6.71 (1H, d, J = 1.6 Hz, 4-H)	3.58 (C $\equiv$ -CH <sub>3</sub> ), 18.93 and 19.30 ((CH(CH <sub>3</sub> ) <sub>2</sub> ), 34.42 (CH(CH <sub>3</sub> ) <sub>2</sub> ), 56.20 (OCH <sub>2</sub> ), 75.48 (C $\equiv$ -CH <sub>3</sub> ), 81.66 (C $\equiv$ -CH <sub>3</sub> ), 86.25 (CH-O), 100.85 (OCH <sub>2</sub> -O), 107.44, 107.63 (C-4, 7), 121.29 (C-6), 134.48 (C-5), 146.88 and 147.63 (C-3a, 7a)

4.10 554	5-[(But-2- ynyloxy)- cyclohexyl- methyl]-1,3- benzodioxole	oil	2920, 2877, 2851, 1610, 1502, 1485, 1441, 1357, 1243, 1132, 1064, 1040, 942.	0.84-1.31 (6H, m), 1.50-1.77 (4H, m) 1.83 (3H, t, $J=2.3$ Hz, $\equiv$ C- CH <sub>3</sub> ), 2.08 (1H, m, H- 1'), 3.76 and 4.01 (ABX <sub>3</sub> , $J_{AB}=15$ Hz, $J_{AX}=J_{BX}=2.3$ Hz, OCH <sub>2</sub> ), 3.98 (1H, d, $J=8.3$ Hz, CH-O), 5.97 (2H, s, OCH <sub>2</sub> O), 6.65- 6.78 (3H, m).	3.64 (C $\equiv$ C-CH <sub>3</sub> ), 25.93 and 26.05 (C-2', C-6'), 26.52 (C-3), 29.25 and 29.86 (C-3', C-5'), 43.97 (C-1'), 56.19 (OCH <sub>2</sub> ), 75.57 (C $\equiv$ C- CH <sub>3</sub> ), 81.64 (C $\equiv$ C- CH <sub>3</sub> ), 85.45 (CH-O), 100.88 (OCH <sub>2</sub> O), 107.47 and 107.64 (C- 4, C-7), 121.31 (C-6), 134.48 (C-5), 146.91 and 147.69 (C-3a, C- 7a).
4.11 555	5-[(But-2- ynyloxy)-phenyl- methyl]-1,3- benzodioxole	oil	2993, 2887, 2859, 1605, 1502, 1486, 1442, 1357, 1239, 1037, 937.	1.89 (3H, t, $J=2.3$ Hz, $\equiv$ C-CH <sub>3</sub> ), 4.12 (2H, q, $J=2.3$ Hz, OCH <sub>2</sub> ), 5.56 (1H, s, CH-O), 5.93 (2H, s, OCH <sub>2</sub> O), 6.74- 6.86 (3H, m), 7.25-7.39 (5H, m)	3.69 (C $\equiv$ C-CH <sub>3</sub> ), 56.34 (OCH <sub>2</sub> ), 75.12 (C $\equiv$ C- CH <sub>3</sub> ), 81.23 (C $\equiv$ C-CH <sub>3</sub> ), 82.56 (CH-O), 100.99 (OCH <sub>2</sub> O), 107.78 and 107.95 (C-4, C-7), 120.98 (C-6), 127.01 (C-2', C-6'), 127.50 (C- 4'), 128.36 (C-3', C-5'), 135.54 (C-5), 141.62 (C-1'), 147.05 and 147.83 (C-3a, C-7a)



	Compound	Mp(C <sup>0</sup> )	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
4.12 493	(2-Butynyloxy- methyl)-3,4- dimethoxy- benzene	oil	3025, 3000, 2956, 2937, 2921, 2855, 2839, 1607, 1595, 1512, 1466, 1443, 1420, 1158, 1140, 1070, 1028	1.84 (3H, t, J=2.3 Hz, C $\equiv$ C-CH <sub>3</sub> ), 3.83 and 3.85 (summa 6H, CH <sub>3</sub> O), 4.08 (2H, q, J=2.3 Hz, OCH <sub>2</sub> C $\equiv$ C-), 4.48 (2H, s, aryl-CH <sub>2</sub> ), 6.77-6.88 (3H, m, aryl)	3.45 (C $\equiv$ C-CH <sub>3</sub> ), 55.67 and 55.71 (CH <sub>3</sub> O), 57.31 (OCH <sub>2</sub> C $\equiv$ C-), 71.22 (aryl-CH <sub>2</sub> ), 75.0 (C $\equiv$ C-CH <sub>3</sub> ), 82.42 (C $\equiv$ C-CH <sub>3</sub> ), 110.76 (C- 2), 111.23 (C-5), 120.54 (C-6), 130.05 (C-1), 148.58 (C-4), 148.88 (C-3).
4.13 503	2,6-Dichloro-1- (2-butyinyloxy- methyl)- benzene	oil	2931, 2918, 2881, 2849, 2241, 1584, 1563, 1473, 1356, 1198, 1157, 1091, 1073, 787, 769	1.87 (3H, t, J=2.3 Hz, $\equiv$ C-CH <sub>3</sub> ), 4.21 (2H, q, J=2.3 Hz, OCH <sub>2</sub> -C $\equiv$ ), 4.83 (2H, s, C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> - O-CH <sub>2</sub> ), 7.17 (1H, dd, J=9.1, 6.7 Hz), 7.31 (2H, m)	3.64 ( $\equiv$ C-CH <sub>3</sub> ), 58.68 (OCH <sub>2</sub> -C $\equiv$ ), 66.15 (C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> -O-CH <sub>2</sub> ), 74.94 (OCH <sub>2</sub> -C $\equiv$ ), 82.81 ( $\equiv$ C-CH <sub>3</sub> ), 128.33 (C-3, C-5), 129.96 (C-4), 133.17 (C-2, C-6), 136.97 (C-1)
4.14 498	1-(2- Butynyloxy)- 1,2,3,4- tetrahydro- naphthalene	oil	2998, 2941, 2860, 1604, 1489, 1440, 1070, 1044	1.84 (3H, t, J=2.3 Hz, C $\equiv$ C-CH <sub>3</sub> ), 3.83 and 3.85 (summa 6H, CH <sub>3</sub> O), 4.08 (2H, q, J=2.3 Hz, OCH <sub>2</sub> C $\equiv$ C-), 4.48 (2H, s, aryl-CH <sub>2</sub> ), 6.77-6.88 (3H, m, aryl)	3.45 (C $\equiv$ C-CH <sub>3</sub> ), 55.67 and 55.71 (CH <sub>3</sub> O), 57.31 (OCH <sub>2</sub> C $\equiv$ C-), 71.22 (aryl-CH <sub>2</sub> ), 75.0 (C $\equiv$ C-CH <sub>3</sub> ), 82.42 (C $\equiv$ C-CH <sub>3</sub> ), 110.76 (C- 2), 111.23 (C-5), 120.54 (C-6), 130.05 (C-1), 148.58 (C-4), 148.88 (C-3)

4.15 479	1-(2- Butynyloxy)- indane	oil	3073, 3000, 2938, 2924, 2854, 2243, 1711, 1667, 1608, 1461, 1332, 1097, 1063, 1018	1.91 (3H, t, $J = 2.3$ Hz, $C\equiv C-CH_3$ ), 2.15 (1H, dddd, $J=13.2, 8.4, 4.8,$ 3.8 Hz, 2-H), 2.37 (1H, dddd, $J=15, 8.4, 6.5, 6.5$ Hz, 2-H), 2.83 (1H, ddd, $J=15.8, 8.4, 4.8$ Hz, 3-H), 3.12 (1H, ddd, $J=15, 7.2, 8.4, 3-$ H), 4.21 (2H, q, $J=2.3$ Hz, $OCH_2$ ), 5.14 (1H, dd, $J=6.5, 3.7$ Hz, 1-H), 7.23 (1H, m), 7.28 (2H, m), 7.45 (1H, d, $J=7$ Hz).	3.52 ( $C\equiv C-CH_3$ ), 30.11 (C-2), 32.25 (C-3), 56.14 ( $OCH_2$ ), 75.45 ( $C\equiv C-CH_3$ ), 81.68 (C- 1), 82.15 ( $C\equiv C-CH_3$ ), 124.80, 125.16 (C-5,6), 126.11, 128.36 (C-4,7), 142.10, 144.14 (C- 3a,7a).
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	Compound	Mp(C <sup>o</sup> )	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
5	4.16 510 2-[(2-Butynyloxy)-methyl]-1,4-benzodioxane	oil	2996, 2921, 2858, 2222, 1594, 1492, 1466, 1269, 1097, 1043	1.87 (3H, t, J=2.4 Hz, . 3.70 and 3.80 (2H, ABX, J <sub>AB</sub> =10.1 Hz, J <sub>AX</sub> =J <sub>BX</sub> =5.0 Hz, CH-CH <sub>2</sub> -O), 4.08 (1H, dd, J=7.6, 11.8 Hz, H-3 $\beta$ ), 4.20 (2H, d, J=2.3 Hz, O-CH <sub>2</sub> -C $\equiv$ ), 4.28-4.41 (2H, m, H-3 $\alpha$ , H-2 $\alpha$ ), 6.81-6.92 (4H, m, C <sub>6</sub> H <sub>4</sub> )	3.57 (H <sub>3</sub> C-C $\equiv$ ), 59.43 (O-CH <sub>2</sub> -C $\equiv$ ), 65.58 (CH-CH <sub>2</sub> -O), 68.12 (C-3), 71.96 (C-2), 74.54 (CH <sub>2</sub> -C $\equiv$ ), 83.22 (H <sub>3</sub> C-C $\equiv$ ), 117.12, 117.40 (C-5 and C-8), 121.37, 121.56 (C-6 and C-7), 143.07, 143.21 (C-4a, C-8a)
15	4.17 539 2-(2-butyryloxy-methyl)-2,3-dihydro-benzofuran	oil	3598, 3478 (broad), 3080, 3040, 2996, 2952, 2871, 1611, 1598, 1481, 1462, 1232, 1092, 1050, 1012, 1004, 954, 899, 865	2.65 (1H, t, J=5.4 Hz, OH), 2.97 and 3.25 (summa 2H, ABX, J <sub>AB</sub> =15.6 Hz, J <sub>AX</sub> =9.4 Hz, J <sub>BX</sub> =7.5 Hz, H-3), 3.79 (2H, m, CH <sub>2</sub> -OH), 4.90 (1H, m, H-2), 6.79 (1H, d, J=8.0 Hz), 6.87 (1H, td, J=7.5, 0.8 Hz), 7.11 (1H, d, J=7.8 Hz), 7.16 (td, J=7.2, 0.5 Hz)	31.18 (C-3), 64.77 (CH <sub>2</sub> -OH), 83.02 (C-2), 109.36 (C-7), 120.54 (C-5), 124.97 (C-6), 126.48 (C-3a), 127.95 (C-4), 159.08 (C-7a)
20					
25					

	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	$[\alpha]_D^{20}$
3	4.18 330 S-(-)-1-[1-(2-butyloxy)-ethyl]-naphthalene	oil	like 4.2 292	(-) 78° (c=1, MeOH)
	4.19 331 R-(+)-1-[1-(2-butyloxy)-ethyl]-naphthalene	oil	like 4.2 292	(+) 155° (c=1, chloroform)
10	4.20 456 S-(-)-2-[1-(2-butyloxy)-ethyl]-naphthalene	oil	like 4.7 293	(-) 190.8° (c=1.0, chloroform)
	4.21 455 R-(+)-2-[1-(2-butyloxy)-ethyl]-naphthalene	oil	like 4.7 293	(+) 199.0° (c=1.17, chloroform)
15	4.22 474 S-(-)-2-[1-(2-propyloxy)-ethyl]-naphthalene	oil	like 4.6 256	(-) 224.4° (c=1.18, chloroform)
20	4.23 475 R-(+)-2-[1-(2-propyloxy)-ethyl]-naphthalene	28-29	like 4.6 256	(+) 228° (c=1, chloroform)

## 5. Aromatic alkyl- alkyl-alkynyl-amine derivatives

## General procedure

The amine was dissolved in dry benzene, the alkynyl bromide was added and the mixture was stirred at room temperature. Then it was diluted with water and ether, the phases were separated, the aqueous phase was twice extracted with ether, the combined organic phases were washed with water, and dried on  $\text{MgSO}_4$ .

	Compound	Mp( $^{\circ}\text{C}$ )	IR ( $\text{cm}^{-1}$ )	$^1\text{H-NMR}$ $\delta$ (ppm)	$^{13}\text{C-NMR}$ $\delta$ (ppm)
5.1 251	N- $\alpha$ -dimethyl- N-2-propynyl- $\beta$ -naphthyl- methylamine	51-53	3173, 3053, 2970, 2941, 2837, 2788, 1600, 1444, 1433, 1371, 1334, 1295, 1227, 1123, 1074, 1011, 969, 952, 935, 900, 863, 827, 754, 734, 713, 557, 482	1.455 (3H, d, CH-Me), 2.271 (1H, s, CCH), 2.360 (3H, s, NMe), 3.253-3.302 and 3.487-3.530 (2H, CH <sub>2</sub> ), 3.708-3.757 (1H, m, CHMe), 7.260-7.834 (7H, m, aromatic)	

## 6. Aryl alkynyl ethers

## General procedure

## 5 A.)

The appropriate phenol was dissolved in dry DMF and to the solution dry  $K_2CO_3$  and the appropriate alkynyl halogenide were added. The reaction mixture was heated to 60°C and stirred at that temperature for 3-6 hours. DMF was then distilled off in vacuo, the residue was taken up in the mixture of  
10 chloroform and distilled water. The phases were separated. the aqueous phase was twice extracted with chloroform. the combined organic phases were washed consecutively with water and saturated sodium chloride solution, dried on  $MgSO_4$  and evaporated. The raw product was purified by chromatography.

## 15 B.)

$Ph_3P$  was dissolved in dry benzene in an inert atmosphere and to the solution the appropriate alcohol and then the phenol were added. The mixture was cooled to 0-10°C. and DEAD (diethyl-azo-dicarboxylate) was added slowly, in small portions. keeping the temperature below 10°C. The reaction mixture was  
20 stirred for 10-24 hours.

Work-up: the precipitated  $Ph_3PO$  was filtered off, the filtrate was washed with water, dried and evaporated. The residue was chromatographed.

## 25 C.)

0.01 mol of phenol were dissolved in 7 ml of dry acetonitrile and under argon atmosphere it was cooled to -4 °C. To the solution were then added 1.968g (0.0129 mol) DBU, keeping the temperature below -4 °C. To the resulting solution 1.8g copper(II)-chloride were added and paralelly the trifluoroacetate  
30 of the other reactant was prepared.

0.0115 mol alkynyl-alcohol were dissolved in 7 ml of acetonitrile, and the solution was cooled to  $-5^{\circ}\text{C}$ , under argon atmosphere. To the solution were added 1.968g (0.0129 mol) DBU, while keeping the temperature below  $-5^{\circ}\text{C}$ . To the mixture were added dropwise 1.6g (0.0115mol) trifluoroacetic  
5 anhydride, keeping the temperature below  $2^{\circ}\text{C}$ . The resulting mixture was stirred at  $0^{\circ}\text{C}$  for 30 mins.

The trifluoroacetate solution thus obtained was added dropwise to the first solution, keeping the temperature below  $0^{\circ}\text{C}$  and the mixture was stirred at  $0^{\circ}\text{C}$  for 5 hours. The reaction was followed by TLC. At the end of the reaction  
10 the acetonitrile was distilled off in vacuo. The residue was shaken with the mixture of 150 ml of benzene and 50 ml of water. The organic layer was washed consecutively with 1N hydrochloric acid, 1N sodium hydroxide, water and saturated sodium chloride solution, then dried and evaporated. The product was purified by chromatography.

15

	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR δ (ppm)	<sup>13</sup> C-NMR δ (ppm)
5	6.1 547 1-(3-butynyloxy)- 4-nitro-benzene	92-94	3287, 3111, 3085, 3075, 2964, 2947, 2920, 1609, 1596, 1510, 1466, 1344, 1333, 1263, 1179, 1110, 1019, 856, 846, 753, 669, 653.	2.07 (1H, t, J=2.6 Hz, C≡C-H), 2.73 (2H, td, J=6.8, 2.6 Hz, CH <sub>2</sub> C≡C), 4.18 (2H, t, J=6.8 Hz, OCH <sub>2</sub> ), 6.97 and 8.18 (summa 4H, dm, J=9 Hz, C <sub>6</sub> H <sub>4</sub> )	19.37 (C≡C-CH <sub>2</sub> ), 66.60 (C≡CH), 70.38 (OCH <sub>2</sub> ), 79.62 (C≡CH), 114.51 (C-2, C-6), 125.89 (C-3, C-5), 141.73 (C-4), 163.40 (C-1)
10	6.2 540 1-(3-pentynyloxy)-4- nitro-benzene	77-78	3067, 3048, 2963, 2917, 2886, 1923, 1607, 1594, 1512, 1467, 1403, 1339, 1260, 1178, 1110, 866, 856, 753, 694, 648, 628, 522, 506.	1.78 (3H, t, J=2.3 Hz, C≡C-CH <sub>3</sub> ), 2.66 (2H, m, CH <sub>2</sub> C≡C), 4.12 (2H, t, J=7.0 Hz, OCH <sub>2</sub> ), 6.95 and 8.18 (summa 4H, dm, J=9 Hz, C <sub>6</sub> H <sub>4</sub> )	3.57 (C≡C-CH <sub>3</sub> ), 19.61 (C≡C-CH <sub>2</sub> ), 67.26 (OCH <sub>2</sub> ), 74.27 (C≡C- CH <sub>3</sub> ), 77.84 (C≡C- CH <sub>3</sub> ), 114.49 (C-2, C- 6), 125.85 (C-3, C-5), 141.59 (C-4), 163.59 (C-1).
20	6.3 377 2,3-dihydro, 2,2- dimethyl-7-(3- butynyloxy)- benzofuran	78-80	3277, 3071, 3043, 2970, 2923, 2889, 2858, 2119, 2022, 1874, 1795, 1714, 1656, 1624, 1611, 1591, 1492, 1470, 1440, 1492, 1396, 1385, 1371, 1302, 1283, 1244, 1201, 1172, 1128, 1077, 999, 972, 946, 887, 838, 780, 753, 720, 682, 663, 635, 600, 546, 502, 458	1.512 (6H, s, diMe), 2.033 (1H, t, CH), 2.710 (2H, m, -CH <sub>2</sub> C), 3.027 (2H, s, CH <sub>2</sub> -ar), 4.206 (2H, t, O-CH <sub>2</sub> ), 6.739-6.815 (3H, m, aromatic)	19.12 (CH <sub>2</sub> -C), 27.88 (diMe), 42.93 (C-3), 66.79 (C-2), 69.61 (O- CH <sub>2</sub> ), 79.96 (CCH), 87.06 (CC), 113.31 (C- 6), 117.86 (C-5), 119.99 (C-4), 128.36 (C-9), 142.62 (C-7), 147.52 (C-8)
25					
30					



6.4 418	2,3-dihydro- 2,2- dimethyl-7-(3- pentynyloxy)- benzofuran	58-59.5	2977, 2963, 2942, 2918, 2880, 2849, 1621, 1591, 1492, 1468, 1389, 1369, 1329, 1305, 1286, 1245, 1203, 1174, 1135, 1115, 1080, 1065, 966, 947, 881, 860, 841, 779, 751, 718, 634, 598, 532, 499.	1.510 (6H, s, diMe), 1.800 (3H, t, Me), 2.627-2.672 (2H, m, - CH <sub>2</sub> C), 3.023 (2H, s, CH <sub>2</sub> -ar), 4.150 (2H, t, O-CH <sub>2</sub> ), 6.751-6.784 (3H, m, aromatic)	3.471 (Me), 19.63 (CH <sub>2</sub> -C), 28.18 (diMe), 43.26 (C-3), 67.54 (C- 2), 74.82 (CC-Me), 77.32 (O-CH <sub>2</sub> ), 87.26 (CC), 113.21 (C-6), 117.87 (C-5), 120.25 (C-4), 128.48 (C-9), 143.12 (C-7), 145.00 (C-8)
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## 7. Alkynyl-oxim-ethers

## General procedure

The oxime was transformed to the oxim-ether in the classical way, by reacting it with the alkynyl bromide in dimethyl formamide, in the presence of potassium carbonate (See method A under the preparation of naphthyl ethers). The raw product was in each case purified by column chromatography.

	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR δ (ppm)	<sup>13</sup> C-NMR δ (ppm)
10					
571	1-Aceto-naphthon-oxim-(2-butyryl)-ether	oil	2990, 2919, 2853, 2230, 1604, 1591, 1459, 1436, 1363, 1353, 1309, 1252, 1034, 1017, 1002, 912	1.94 (3H, t, J=2.3 Hz, CH <sub>3</sub> -C≡), 2.41 (3H, s, CH <sub>3</sub> -C=N), 4.84 (2H, q, J=2.3 Hz, O-CH <sub>2</sub> ), 7.46-7.57 (4H, m), 7.87 (2H, m), 8.15 (1H, m)	3.80 (CH <sub>3</sub> -C≡), 17.51 (CH <sub>3</sub> -C=N), 62.25 (O-CH <sub>2</sub> ), 75.33 (CH <sub>2</sub> -C≡), 82.75 (CH <sub>3</sub> -C≡), 125.15, 125.46 (C-6, C-7), 125.96 (C-3), 126.01 (C-3), 126.49 (C-2), 128.40 (C-5), 129.10 (C-4), 130.85 (C-1), 133.86 (C-4a), 135.27 (C-8a), 157.41 (CH <sub>3</sub> -C=N)
15					
20					
25	3,4-Dimethoxy-acetophenonoxy m-(2-butyryl)-ether	85	3080, 3003, 2963, 2929, 2869, 2840, 2237, 1595, 1577, 1518, 1447, 1417, 1337, 1311, 1278, 1249, 1234, 1176, 1153, 1030, 937, 879, 804, 768, 634, 621	1.87 (3H, t, J=2.3 Hz, CH <sub>3</sub> -C≡), 2.23 (3H, s, CH <sub>3</sub> -C=N), 3.88 and 3.90 (CH <sub>3</sub> O), 4.75 (2H, q, J=2.3 Hz, O-CH <sub>2</sub> ), 6.83 (1H, d, J=8.4 Hz), 7.15 (1H, dd, J=8.4, 2 Hz), 7.29 (1H, d, J=2 Hz)	3.77 (CH <sub>3</sub> -C≡), 12.76 (CH <sub>3</sub> -C=N), 55.86 (CH <sub>3</sub> O), 62.23 (O-CH <sub>2</sub> ), 75.27 (CH <sub>2</sub> -C≡), 82.53 (CH <sub>3</sub> -C≡), 108.8 (C-5), 110.51 (C-2), 119.28 (C-6), 129.18 (C-1), 148.78 (C-3), 150.14 (C-4), 155.0 (CH <sub>3</sub> -C=N)
30					

Activity results:Example 1.

Investigation of synergistic activity on house fly (*Musca domestica*) following topical application

In two parallel experiments 10 female, 2-4 day old house flies were treated on the ventral side of their thorax with 0.2  $\mu$ l of the test solution, with the help of Hamilton MicroLab P microdispenser. Beside *fixed synergist dose of 1000 ng/fly* the animals were treated with carbofuran at a dose of 20 ng/fly. For solvent cellosolve was used. Selection and counting of the flies were performed under the action of CO<sub>2</sub>. After treatment the flies were kept in plastic cups covered with tulle. Mortality after 24 hours was expressed in %. Results are demonstrated in the table below:

Material	Carbofuran-synergist (ng/fly)	
	20+0	20-1000
	mortality %	
<i>Alkyl esters, amides, imides</i>		
501	3	53
502	0	47
523	0	17
535	3	27
541	0	46
542	0	42
<i>Aryl-alkyl-alkynyl ethers</i>		
279	0	72
256	0	32
441	1	97
484	0	63
493	1	100
599	10	100
503	0	95
292	0	72
293	0	45

454	0	75
472	1	68
479	1	58
330	0	62
331	0	72
455	0	70
456	0	47
389	2	27
554	0	58
555	0	90
539	0	48
474	0	50
510	2	75
498	5	70
475	0	47
Aromatic alkyl- alkyl-alkynyl- amine derivatives		
251	2	37
Aryl alkynyl ethers		
547	0	47
540	0	60
377	0	57
418	0	63
Aralkyl-aldoxime, ketoxime-alkynyl ethers		
571	0	53
572	0	55

### Example 2.

Investigation of synergistic activity on cotton bollworm (*Helicoverpa armigera*) following topical application

Treatment was performed similarly as described in Example 1. but L2 stadium grubs of cotton bollworms (*Helicoverpa armigera*) were treated as test animals. From the 24 hour dose - mortality data the LD<sub>50</sub> (ng/grub) values were

determined using probit analysis. None of the synergists acted at the applied 1000 ng/grub dose. Synergist ratio was calculated as the quotient of the LD<sub>50</sub> values of carbofuran administered alone, and with the synergist. The experiments were performed in 2-4 replica. Synergist ratios are demonstrated in the table below:

Materials	Synergist ratio
<i>Alkynyl-esters, amides</i>	
501, 502, 523, 535, 541, 542, 537	>5
<i>Aryl-alkyl alkyl-alkynyl ethers</i>	
279, 256, 441, 484, 493, 503, 292, 293, 454, 510, 475, 498, 479, 472, 331, 455, 456, 389, 554, 555, 539, 474, 330, 599	>5
<i>Aromatic alkyl- alkyl-alkynyl-amine derivatives</i>	
251	>5
<i>Aryl alkynyl ethers</i>	
540, 377, 418	>5
<i>Alkynyl-oximethers</i>	
571	
572	>5

### Example 3.

Investigation of synergist spectrum on house fly (*Musca domestica*) and cotton bollworm (*Helicoverpa armigera*) following topical administration

Synergistic activities of materials No. 279 and 599 of the present invention for various active ingredients were determined on house fly (*Musca domestica*) and cotton bollworm (*Helicoverpa armigera*) using methods of treatments as described in biological Examples 1 and 2. For the active ingredients ISO

common names are given (see: Pesticide Manual 1994). The obtained synergist ratios are shown below:

5	active ingredient	279		599	
		Musca domestica	Helicoverpa armigera	Musca domestica	Helicoverpa armigera
10		Synergist ratio		Synergist ratio	
	carbofuran	>20	>10	>40	>20
	bendiocarb	>20	>10	>40	>20
	isoprocarb	>40	-	>40	>20
	fenobucarb	>10	-	>20	-
	aminocarb	>20	-	>20	-
	thiodicarb	>10	-	>10	-
	methomyl	>10	-	>10	-
15	pirimicarb	>20	-	>20	-
	dioxacarb	>20	-	>40	>20
	propoxur	>20	>10	>40	>20
	imidacloprid	>5	-	>5	-
	lindan	>5	>5	-	-
20	azinphosmethyl	>5	>5	-	-
	chlorpyrifos	>5	>5	-	-
	esbiol	>5	-	>10	-
	permethrin			>5	>10
	tetramethrin			>5	-

Example 4.

Effect of the active ingredient:synergist ratio on the synergistic activity

5 Treatment was performed as described in Example 1. using Hamilton MicroLab  
P microdispenser. In two parallel experiments 10 female, 2-3 day old flies were  
treated on the ventral side of their thorax with 0.2  $\mu$ l test solution. Beside 1000-  
400-200-80 ng/fly fixed doses of the synergist they were treated with *constant*  
20 ng/fly *carbofuran*. Selection and counting of the flies were performed under  
10 the action of CO<sub>2</sub>. After treatment the flies were kept in plastic cups covered  
with tulle. After 24 hours mortality % was recorded. Depending on the results  
the experiments were performed in 2-4 replica. Results are demonstrated in the  
table below.

20

25

30

Materials	Dose of the Synergist (ng/fly)				
	0	80	200	400	1000
	24 hour mortality (%)				
501	0	60	75	80	80
441	0	62	67	90	95
493	0	75	88	94	100
503	0	37	50	65	93
454	0	40	45	60	75
455	0	25	48	63	77
599	0	65	90	95	100

Example 5.

Investigation of synergistic activity on resistant house fly (*Musca domestica*) populations

The table below demonstrates synergistic activities of materials of the present invention for various active ingredients on two resistant house fly strains (INSEL, IX). Investigation was carried out as described in biological Example 1. LD<sub>50</sub> values and synergist ratios were determined as given in Example 2.

Treatment	INSEL strain		IX strain	
	LD <sub>50</sub> (ng/fly)	SR	LD <sub>50</sub> (ng/fly)	SR
carbofuran	15375		>100000	
+ 279	29	530	94	4760
methomyl	475		851	
+ 279	46	10	109	5
pirimicarb	>100000		>100000	
+ 279	696	145	3562	115
aldicarb	695		2104	
+ 279	172	4	507	4
bendiocarb	100000		100000	
+ 279	150	667	746	134
isoprocarb	>100000		>100000	
+ 279	983	102	2145	47
esbiol	10653		-	
+ 279	794	13	-	-



Example 6.

Investigation of synergistic activity on oat aphid (*Rhopalosiphum padi*)

5 5-8 cm high oat plants, sawn in plastic cups were infected with different aged specimens of *Rhopalosiphum padi* aphids. The settled aphids were counted before the treatment, then the plants were sprayed, using a hand sprayer, with 1 ml of the spray solution, beside the *administration of fixed dose (30 ppm) of the synergist*. Of compound No. 279 of the present invention a 100 g/l concentration emulgeable concentrate was prepared, by methods usual in the  
10 formulation praxis, applying solvent and surface active materials. Test solutions used for the spraying were prepared from this concentrate and from marketed preparations by dilution. Mortality of the aphids was determined 24 hours after the treatment. Results are shown below:

15

Treatment	Mortality %
carbofuran 1 ppm	<.50
carbofuran 1 ppm + 279	> 95
pirimor 2 ppm	< 30
20 pirimor 2 ppm + 279	> 95
imidacloprid 0.1 ppm	< 50
imidacloprid 0.1 ppm - 279	> 95

Example 7.

25 Investigation of the effect on fecundity, on house fly (*Musca domestica*)

Groups consisting of freshly hatched 50 male and 50 female flies were fed during 48 hours with granulated sugar comprising 500 ppm of material No. 441  
30 and 484 of the present invention respectively, and the eggs layed on the next 10 days were raised. The fecundity-hindering effect was expressed as the quotient

of the emerged flies in the treated and untreated groups. The experiments were performed in 4 replica.

Treatment	Hindering effect on fecundity
441	87 %
484	90 %

### Example 8.

Synergism of acaricidal effect investigated on two-spotted spider mite (*Tetranychus urticae*)

From the first pair of leaves of a 1 week old bean plant leaf-discs of 225 mm diameter were cut which were treated by dipping them (5 min) into the test solution consisting of the active ingredient and the synergist in definite concentrations. For the preparation of the stock solutions of required concentration, 10 % acetone as co-solvent and 0.1 % Tween-80 as detergent were applied. The dried leaf-discs were placed on wet surface and they were infected with 10 grown-up female mites per leaf. After 48 hours the mortality was recorded using microscope and a brush. The experiment was performed in 4 replica. Averages of the results are shown in the table below.

<i>Treatment with the active ingredients alone</i>	Concentration (ppm)				
	31	62	125	250	500
	Mortality %				
279	0	6	8	18	30
carbofuran	13	39	44	81	90
bromopropylate	18	28	90	-	-
<i>Treatment with the active ingredients in combinations</i>	Concentration (ppm)				
	16+16	31+31	62+62	125+125	250+250
	Mortality %				
279+carbofuran	29	80	80	100	100
279+bromopropylate	75	90	100	-	-

Example 9.

Efficacy in field trial against Colorado potato beetle (*Leptinotarsa decemlineata*)

5 Of compound No. 279 of the present invention a 100 g/l concentration emulgeable concentrate was prepared by methods usual in the formulation praxis. applying solvent and surface active materials. Chinufur 40 FW composition. comprising 400 g/l carbofuran was applied together with a fixed dose of 2 l/ha of compound No. 279. in a small plot field study against Colorado  
10 potato beetle (*Leptinotarsa decemlineata*). Spraying was carried out with motoric sprayer (Maruyama) applying 300 l/ha spray solution. Treatments were performed in 4 replica. on plots of 25 m<sup>2</sup>. The effect of the treatments was evaluated on the 2nd day by counting the surviving beetles on the plants. Results are shown in the table below:

15

20

Treatment	Dose (l/acre)	carbofuran:279 ratio	Number of potato beetles piece/plant	
			before treatment	after treatment
untreated	-	-	23.6	28.0
Chinufur 40 FW	0.1	1:0	18.4	6.1
Chinufur 40 FW	0.2	1:0	32.0	6.8
Chinufur 40 FW+279	0.1+2.0	1:5	21.3	0.4

Example 10.

Synergist activity of compound Nr. 599

Synergist activity of compound 599 with various specific acaricides was investigated against two-spotted spider mite (*Tetranychus urticae*), by the method described in Example 8. The  $LC_{50}$  and  $LC_{95}$  values calculated from the concentration-mortality relationship are shown in the table below.

Synergist activity against two-spotted spider mite (*Tetranychus urticae*)

Treatment	Ratio of Acaricide/ Synergist	Exposure time (h)	$LC_{50}$	$LC_{95}$	Synerg ratio	
			(mg /l)		$SR_{50}$	$SR_{95}$
Carbofuran	1:0	24	163.9	799.9	-	-
Carbofuran+MB-599	1:1	24	55.5	286.8	3.0	2.8
	1:2	24	33.5	93.7	4.9	8.5
	1:4	24	27.5	67.0	6.0	11.9
Fenazaquin	1:0	3	>1000	-	-	-
	1:0	24	41.9	801.3	-	-
Fenazaquin + PBO	1:1	3	326.7	>1000	>3.1	-
	1:1	24	20.4	371.8	2.1	2.2
Fenazaquin+MB-599	1:1	3	68.1	280.2	>15	-
	1:1	24	31.3	174.8	1.3	4.6
Tebuufenpyrad	1:0	3	>1000	-	-	-
	1:0	24	63.4	>1000	-	-
Tebuufenpyrad +PBO	1:1	3	115.9	1081	>9	-
	1:1	24	35.7	118.0	1.8	>8.5
Tebuufenpyrad+MB599	1:1	3	61.8	658.7	>16	-
	1:1	24	22.3	141.8	2.8	>7.0

Example 11.

Synergist activity against pea aphid (*Acyrtosiphon pisum*)

Synergist activity of compound No. 599 was tested against pea aphid (*Acyrtosiphon pisum*) in field trials on small plots (10 m<sup>2</sup>). 300 l/ha spray volume was applied using motoric sprayer (Maruyama). Efficacy was expressed by the average number of aphids/leaf before, and two days after the treatment, respectively. (Henderson and Tilton: J. Econ. Entomol., 48:157, 1955). Results are shown in the table below.

Treatment	Dose act. ingr./ha.	E (%)
Pirimicarb	250	93.8
	80	86.3
Pirimicarb + MB-599	80+80	95.5
Fipronil	240	94.6
Fipronil + MB-599	120+120	95.7
Carbofuran	160	99.1
	110	98.0
Carbofuran + MB-599	110+110	100.0
Triazamate	50	96.8
Triazamate + MB-599	33+33	97.7
Imidacloprid	120	98.4
Imidacloprid+MB-599	120+120	100.0

Example 12.

Comparative investigations with known reference synergists

LD<sub>50</sub> values of the reference compounds were determined in 4 replica on flies treated with carbofuran and 1000 ng of the known synergist, and the SR<sub>50</sub> ratios were counted in relation to the control carbofuran. These SR<sub>50</sub> ratios were

compared to those of the new compounds prepared by us. Our compounds were more active in each case.

1. Alkynyl esters

known

according to the  
invention

Synergist ratio	2-propynyl 1-naphthyl-carboxylate	502
SR <sub>50</sub>	4.11	6.28

2. (Aryl-alkyl), alkyl-alkynyl ethers

known

according to the  
invention

Synergist ratio	(2,6-dichlorophenyl)methyl 2-propynyl ether	503
SR <sub>50</sub>	20.92	21.16

known

according to the  
invention

Synergist ratio	5-[(2-propynyl)-methyl]-1,3-benzodioxole	441
SR <sub>50</sub>	10.60	25.70

known

according to the  
invention

Synergist ratio	1-naphthylmethyl 2-propynyl ether	279
SR <sub>50</sub>	5.28	28.7

known

according to the  
invention

Synergist ratio	2-[(2-propynyloxy)methyl]-1,4-benzodioxane	510
SR <sub>50</sub>	5.58	18.32

known

according to the  
invention

Synergist ratio	(2-propynyloxy-methyl)-3,4-dimethoxy-benzene	493
SR <sub>50</sub>	6.58	32.84

## 3. Aryl alkynyl ethers

known

according to the  
invention

Synergist ratio	2,3-dihydro-2,2-dimethyl-7-(2-propynyloxy)benzofurane	418
SR <sub>50</sub>	1.8	20.5

Known naphthyl alkynyl ether	Synergist ratio SR <sub>50</sub>
1-naphthyl 2-propargyl ether	6.52
1-naphthyl 3-butyryl ether	7.95
2-naphthyl 2-butyryl ether	7.72
2-naphthyl 3-pentyryl ether	9.97

## 4. Alkynyl-oxim-ethers

known

according to the  
invention

Synergist ratio	1-acetonaphthon-oxim (2-propynyl) ether	571
SR <sub>50</sub>	7.79	10.02

Examples for formulation:

Names of the marketed auxiliary materials are given in quotation marks.  
followed by the makers name.

5

## 1. Preparation of powders

## A)

To 158g of fine-grained perlite 20g of carbofuran and 20g of compound 279,  
10 were mixed in a homogenizator to this mixture were added 2g of fatty alcohol  
polyglycol ether ("G-3920" ICI) and the mixture was homogenized. The powder  
mixture was grained in an ejector mill and to it were added 5g of octyl-phenol-  
polyglycol-ether (EO=20) ("Triton X-165" Rohm & Haas) and 2g of alkyl-  
sulfosuccinate ("Aerosol-13" Cyanamid). The resulting product is a wettable  
15 powder mixture (WP).

## B)

10g of compound 279 and 10g of carbofuran were diluted with 2g of ethanol.  
20 The solution was mixed in a powder homogenisator with 5g of calcium-lignin-  
sulfonate ("Borrespeseca" Borregard), 5g of nonyl-phenol-polyglycol-ether  
(EO=20) ("Arkopal N-200" Hoechst), and 70g of calcium carbonate. The  
resulting product was grained in an alpine-100 typ mill. Average particle size  
was 1-2  $\mu\text{m}$ . This composition may be used to prepare microsupensions.

25

## C)

The mixture of 3g of Diazinon, 3g of compound 441, and 0.3g of fatty alcohol-  
polyglycol-ether ("G-3920" ICI) was taken up in a homogenisator apparatus on  
30 the mixture of 1.0g synthetic silicic acid (Aerosil 200) and 191g talc ( $d_{\text{max.}}=15\text{-}$   
30  $\mu\text{m}$ ), the pH of the latter was previously adjusted to pH=7.0 with potassium-



and sodium-phosphate buffer. Under further stirring 1g of dioctyl-sulfosuccinate ("Aerosol OTB" Cyanamid) and 1g of fatty alcohol-polyglycol-ether-sulfonate ("Genapol LRD" Hoechst) were added and finally the mixture was grained to an average particle size of 20  $\mu\text{m}$ . The resulting product is an easy  
5 flowing powder preparation.

## 2. Preparation of emulsion concentrates

### 10 A)

The mixture of 5g of pirimicarb and 5g of compound 493 was dissolved in the mixture of 20g of xylene and 40g of propanol. To this solution was added the mixture of 4g of ethoxylated alkyl-phenol + lineare alkyl-aryl-sulfonate-calcium salt ("Geronol FF/U Geronazzo) and 6g of ethoxylated amine + fatty acid +  
15 lineare alkyl-aryl-sulfonate alkali metal salt ("Geronol MS" Geronazzo). After complete dissolution 20g of water were added. Transparent solution was obtained, for which is characteristic, that on dilution with water it forms an emulsion of 0.8-1.5  $\mu\text{m}$  drop-diameter.

### 20 B)

The mixture of 5g of quinalphos and 10g of compound 484 and the mixture of 7g of ethoxylated-(EO=13)-propoxylated-(PO=21)-nonylphenol, 2g of lineare-dodecylbenzenesulfonic acid-calcium salt and 12g POE-(20)-sorbitan-monooleate were dissolved in the mixture of 28.6-28.6 ml of propyleneglycol  
25 and pine-fatty acid and 23.8ml of sun-flower oil, 9.5ml of etanol and 95 ml of aliphatic hydrocarbone with 45% naphthene content. The material thus obtained may be preferably used for the preparation of microemulsions.

### C)

30 The mixture of 0.02-0.02 parts by mass of the active ingredient and of the synergist is dissolved in 10 parts by mass of propanol, to the resulting solution

99.96 parts by mass of odourless petroleum are added and the mixture is stirred until a homogenous solution is obtained. The resulting oily dispersible preparation can directly be used in ULV applications.

5 D)

The method described in example A) is followed, with the difference that 10g of compound 279 is applied as synergist active ingredient.

10 3. Preparation of granulates

In a mechanical granulator are mixed 300g of carbofuran, 300g of compound 418, 1500g of polycarboxylate alkali salt ("Sorphol." Toho), 500g of dodecylbenzenesulfonic acid sodium salt ("Marlon TP 370" Hüls), 500g of beet sugar and 7200g of caolinite. The powder mixture thus obtained is mixed with 8300ml  
15 of water using a mixer of high shear force ( $v=10\text{m/s}$ ). The mixture is finally spray-dried. Particle-size distribution of the product is 0.1-0.4 mm.

4. Preparation of aerosols

20

In a 100 l apparatus supplied with stirrer are mixed 1kg of bioallethrin, 0.5kg of compound 441, 0.1kg of aerosil-air 972, 0.1 kg of ethyleneglycol-monosalicylate, 15kg of odourless petroleum and 50kg of propanol. After dissolution it is filled into cylinders with 33.3kg of liquid propane-butane  
25 (25-75) gas.

### 5. Preparation of vaporators

In 60 ml of ethanol are dissolved 5g of S-bioallethrin, 5g of compound 279 and 1 g of lemon aroma. The solution is applied in vaporators, at a temperature of 50 °C.

**What we claim is:**

1.) Compounds of the general formula I, their optically active isomers and salts  
- wherein

5 Ar = alicyclic, aromatic or one or more heteroatom containing heterocyclic moiety, optionally substituted by one or more alkoxy-, methylenedioxy-, alkyl-, halogen-, haloalkyl-, or nitro-group and/or condensed with a benzene ring;

R<sup>1</sup>, R<sup>2</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl,

10 R<sup>3</sup>, R<sup>4</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, or

R<sup>3</sup>, R<sup>4</sup> are together =O,

Y = C; PO, or

15 YR<sup>3</sup>R<sup>4</sup> together  $\begin{array}{c} \text{R}^9 \\ | \\ -\text{C}=\text{N}- \end{array}$  group;

X = -O-, -NR<sup>10</sup>,

R<sup>9</sup> = H, alkyl, phenyl, substituted phenyl;

R<sup>10</sup> = H, alkyl;

R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> are independently H, alkyl, alkenyl, haloalkyl, or

20 Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(YR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X- form together a carboximide group;

E = H, halogen, methyl;

m = 0, 1, 2 ;

n = 0, 1 ;

o = 0, 1, 2 ;

25 p = 0, 1, 2,

with the proviso, that the sum of the atoms or groups of the -(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X-(CR<sup>5</sup>R<sup>6</sup>)<sub>o</sub>-(CR<sup>7</sup>R<sup>8</sup>)<sub>p</sub> bridge skeleton is 3 and the -C≡C-E skeleton forms with the atoms of the bridge a linear chain, consisting of 6 atoms ending preferably in a methyl group,

furthermore with the proviso, that if Ar stands for a naphthyl group. Y means C-atom. X means O-atom. R<sup>3</sup> and R<sup>4</sup> together can not mean =O.

2.) Compounds of general formula IA and their optically active isomers - where  
5 Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o and p have the same meanings as defined in claim 1.

3.) Compounds of general formula IB and their optically active isomers - where  
10 Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, Y, E, m, o and p have the same meanings as defined in claim 1.

4.) Compounds of general formula IC and their optically active isomers - where  
15 Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o and p have the same meanings as defined in claim 1.

5.) Compounds of general formula ID and their salts and optically active  
isomers - where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, E, m, n, o and p  
have the same meanings as defined in claim 1.

20 6.) Compounds of general formula IE and their salts and optically active isomers  
- where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, E, m, n, o and p have the  
same meanings as defined in claim 1.

7.) Compounds of general formula IF and their optically active isomers - where  
25 Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, o and p have the same meanings as  
defined in claim 1.

8.) Compounds according to claim 1.

1-naphthylmethyl 2-butyryl ether,

30 2-propynyl-1,3-benzodioxol-5-carboxylate,  
1-[(2-butyryloxy)-ethyl]-3,4-dimethoxybenzene,

2,6-dichloro-1-(2-butynyloxy-methyl)benzene.

1-[1-(2-butynyloxy) propyl]naphthalene.

R-(+)-2-[1-(2-butynyloxy) ethyl]naphthalene.

5-[(but-2-ynyloxy)methyl]-1,3-benzodioxole.

5-[2-methyl-1-(2-butynyloxy)propyl]-1,3-benzodioxole.

5-[(but-2-ynyloxy)phenylmethyl]-1,3-benzodioxole

2-[(2-butynyloxy) methyl]-1,4-benzodioxane.

2,3-dihydro-2,2-dimethyl-7-(3-pentyloxy)benzofurane.

10 9.) Process for the preparation of compounds of general formula I. where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, X, Y, E, m, n, o, and p, have the same meanings as defined in claim 1.

characterized by, that

15 a.) for the preparation of compounds of general formula IA, where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meanings as defined in claim 1.,

compounds of general formula II and III are reacted, where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meanings as defined in claim 1.,

20 A and B are groups suitable to form ester bond.

b.) to prepare compounds of general formula IB, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, Y, E, m, o, and p, have the same meanings as defined in claim 1.,

25 compounds of general formula IV and V are reacted, where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meanings as defined in claim 1., and C and D are groups suitable to form amide bond.

30 c.) to prepare compounds of general formula IC, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meanings as defined in claim 1., R<sup>3</sup> and R<sup>4</sup> independently mean H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl,

compounds of general formula VI and VII are reacted. wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p have the same meanings as defined in claim 1.. R<sup>3</sup> and R<sup>4</sup> independently mean H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl. F and G are groups suitable to form ether bond.

5

d.) to prepare compounds of general formula ID, wherein Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>2</sup>R<sup>4</sup>)<sub>n</sub>-N- stands for a carboximide group, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, o, and p, have the same meanings as defined in claim 1..

the carboximide of general formula VIII is reacted with the compound of  
10 general formula IX, wherein R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, o, and p, have the same meanings as defined in claim 1. and Lg represents a leaving group,

e.) to prepare compounds of general formula IE, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, E, m, n, o, and p, have the same meanings as defined in  
15 claim 1.,

compounds of general formula X and XI are reacted. wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meanings as defined in claim 1., H and I represent groups, suitable to form a  
-N-

20 R<sup>10</sup>

group where the meaning of R<sup>10</sup> is the same as defined in claim 1..

f.) to prepare compounds of general formula IF, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, o, and p, have the same meanings as defined in claim 1..  
25 compounds of general formula XII and IX are reacted. where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, n, o, and p, have the same meanings as defined in claim 1.. and Lg represents a leaving group, and

if desired, the compound of general formula I thus obtained is transformed into  
30 its salts, or liberated from its salts, and, if desired, the optically active isomers are separated.

10.) Pesticide composition comprising as active ingredient 0.0001-99.9 % by mass of a compound of the general formula I,

where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, m, n, o and p have the same meanings as defined in claim 1.,

and optionally other pesticide active ingredient(s), beside carriers and other auxiliary materials.

11.) Arthropodicide composition comprising as active ingredient 0.0001-99.9 % by mass of a compound of the general formula I,

where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, m, n, o and p have the same meanings as defined in claim 1.,

and optionally other arthropodicide active ingredient(s), beside carriers and other auxiliary materials.

12.) Composition according to claim 11, characterized by, that it contains as other active ingredient

Acetamide derivatives: e.g. oxamyl;

Benzoylurea compounds: e.g. flucycloxuron, hexaflumuron, teflubenzuron, triflumuron;

Benzoylurea like IGR compounds;

Bicycloheptadien compounds: e.g. heptenophos;

Cross-bridged diphenyl compounds: e.g. etofenprox, bromopropylate, methoxychlor, temephos, tetradifon;

Carbamates: e.g. aminocarb, aldicarb, aldoxycarb, asulam, bendiocarb, benfuracarb, carbaryl, carbetamide, carbofuran, carbosulfan, diethofencarb, dioxacarb, ethiofencarb, fenobucarb, fenoxycarb, furathiocarb, isoprocarb, methomyl, oxamyl, pirimicarb (pirimor), propoxur, thiodicarb, thiofanox, xylylcarb;

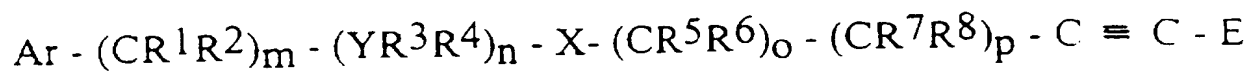
Carbamoyloxime derivatives: e.g. alanycarb, butocarboxim;

Cyclodienes: e.g. aldrin, chlordane, endosulfan, heptachlor;

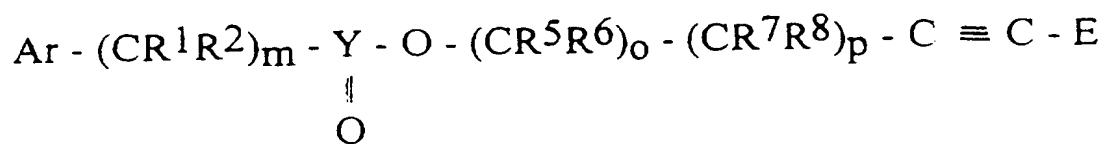


- Diazoles: fipronil;  
Hydrazides: RH 5992, RH 5849, CGA 215'944;  
Nereistoxin analogues: pl. bensultap;  
Nitroimidazolidinylenamines: e.g. imidacloprid;
- 5 Organophosphor compounds e.g. quinalphos, diazinon, phosalone, dimethoate, azinphos-methyl.  
Organotin compounds e.g. azocyclotin, cyhexatin, fenbutatin oxide SSI-121;  
Phenoxy compounds: e.g. diafenthiuron;  
Pyrazoles: e.g. pyrazophos;
- 10 Pyrethroides: e.g. allethrin, bioallethrin (esbol), acrinathrin, fenvalerate, empenethrin, prallethrin, resmethrin, MTI-800, flufenprox, permethrin, tetramethrin, cypermethrin and their isomers and isomer-combinations;  
Pyridazinones: e.g. pyridaben;  
Pyridine derivatives: e.g. chlorpyrifos;
- 15 Pyrimidine derivatives: e.g. pyrimiphos-ethyl, pyrimiphos-methyl;  
Pyrroles: e.g. AC 303-t, 630;  
Quinazolines: e.g. fenazaquin;  
Terpenoid derivatives: e.g. methoprene;  
Tetrazines: e.g. clofentezine, SzI-121 (flufenzin);
- 20 Thiadiazines: e.g. buprofezin;  
Thiazolidin: pl. hexythiazox;  
Triazoles: pl. isazophos, RH 7988;  
Chlorinated hydrocarbons: lindane;  
Macrocyclic lactones;
- 25 Tebufenpyrad;  
Fenpyroximate;  
Triazamate;
- 13.) Compositions according to claims 11. and 12, comprising a s active  
30 ingredient of general formula I one or more of the following compounds:  
1-naphthylmethyl 2-butyryl ether,

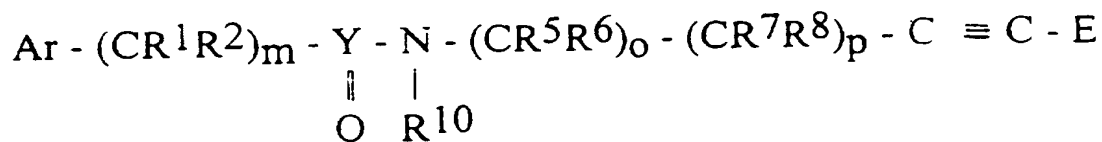
- 2-propynyl-1,3-benzodioxol-5-carboxylate.  
1-[(2-butynyloxy)-ethyl]-3,4-dimethoxybenzene.  
2,6-dichloro-1-(2-butynyloxy-methyl)benzene.  
1-[1-(2-butynyloxy)propyl]naphthalene.  
5 R-(+)-2-[1-(2-butynyloxy)ethyl]naphthalene,  
5-[(but-2-ynyloxy)methyl]-1,3-benzodioxole.  
5-[2-methyl-1-(2-butynyloxy)propyl]-1,3-benzodioxole.  
5-[(but-2-ynyloxy)phenylmethyl]-1,3-benzodioxole.  
2-[(2-butynyloxy)methyl]-1,4-benzodioxane.  
10 2,3-dihydro-2,2-dimethyl-7-(3-pentyloxy)benzofuran.
- 14.) Composition according to claims 11-14 comprising as active ingredient 0.0001-99.9 % by mass of a compound of the general formula I. where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, m, n, o and p have the same meanings as  
15 defined in claim 1., and a carbamate suitable for extermination of arthropoda, preferably carbofuran.
- 15.) Composition according to claim 14 containing (2-butynyloxy-methyl)-3,4-dimethoxybenzene, as compound of the general formula I.  
20
- 16.) Composition according to claim 14 containing 5-[(but-2-ynyloxy)methyl]-1,3-benzodioxole, as compound of the general formula I.
- 17.) Process for extermination of pests, preferably arthropoda, comprising  
25 treating pests, preferably arthropoda with a suitable amount of a composition of claims 10 or 11, if desired in such a way that the compositions containing compounds of the general formula I, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, m, n, o and p have the same meanings as defined in claim 1., and the compositions containing the known active ingredients are used in a tank  
30 mixture or subsequently.



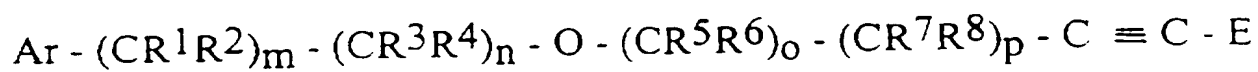
I.



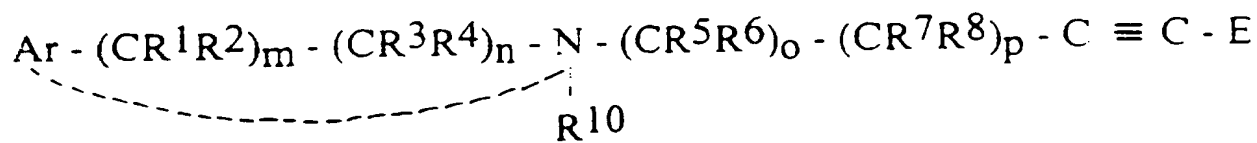
IA



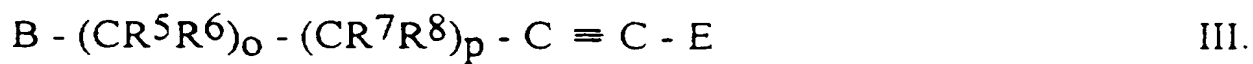
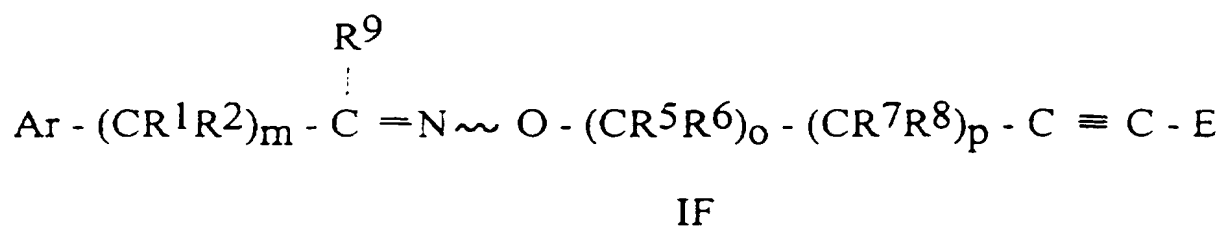
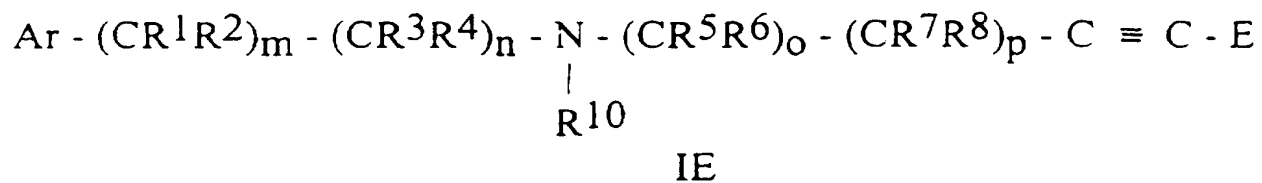
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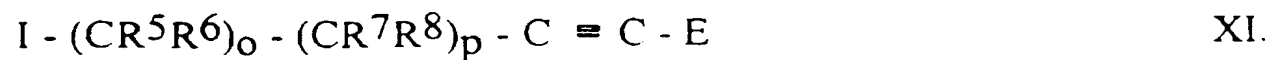
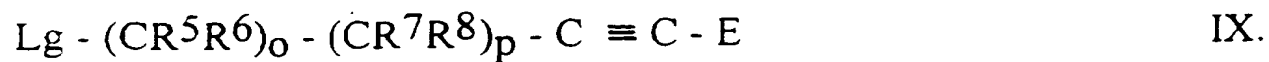
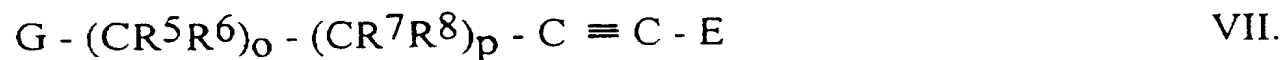
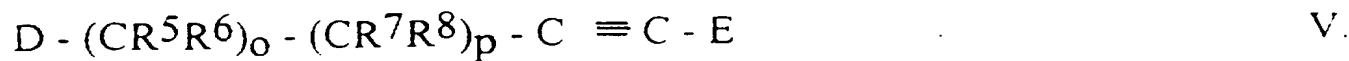


IC



ID





# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/HU 96/00069

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C43/166 A01N31/04 C07C43/215 C07C43/176 C07D317/48  
C07D307/79 C07D319/20 A01N31/16 A01N43/30 A01N43/32  
A01N43/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, vol. 16, no. 5, 1968, WASHINGTON US, pages 779-786, XP002029949 R. M. SACHER ET AL: "Propynyl naphthyl ethers as selective carbamate synergists" cited in the application see Table I, compound no. XIII and Fig. 1 ---	1,4, 9-12,17
X	US 3 954 793 A (D. J. HENNESSY) 4 May 1976  see column 2, line 32 - column 4, line 55; examples 1,2,5,6 & DE 22 35 005 A cited in the application ---	1,4,7, 9-12,14, 17
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*G\* document member of the same patent family

Date of the actual completion of the international search

28 April 1997

Date of mailing of the international search report

26.05.97

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/HU 96/00069

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 718 686 A (M. S. CHODNEKAR) 27 February 1973 see column 4, line 3 - column 7, line 24; examples 44-48	1,2,4, 9-11,17
X	US 3 402 179 A (K. F. MINOO-SHI) 17 September 1968 see example 1; table 1 & NL 6 600 916 A cited in the application	1,5, 9-12,17
A	GB 2 161 163 A (KUREHA KAGAKU KOGYO) 8 January 1986 see claims	1,2, 9-11,17

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/HU 96/00069

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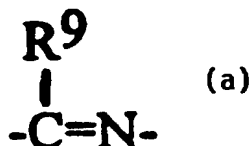




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/HU96/00069 (22) International Filing Date: 19 November 1996 (19.11.96) (30) Priority Data: P 95 03318 21 November 1995 (21.11.95) HU (71) Applicant (for all designated States except US): CHINOIN GYÓGYSZER ÉS VEGYÉSZETI TERMÉKEK GYÁRA RT. [HU/HU]; Tó u. 1-5, H-1045 Budapest (HU). (72) Inventors; and (75) Inventors/Applicants (for US only): ARVAI, Géza [HU/HU]; Róbert K. krt. 20, H-1138 Budapest (HU). BAKONYVÁRI, Ildikó [HU/HU]; Damjanich u. 4/a, H-8200 Veszprém (HU). BERTÓK, Béla [HU/HU]; Rizling u. 16, H-1223 Budapest (HU). CSÍZ, László [HU/HU]; Tulipán u. 5, H- 2030 Érd (HU). CZUDOR, Irén [HU/HU]; Kiránduló u. 1/a, H-1222 Budapest (HU). KURUCZNÉ, R., Zsuzsa [HU/HU]; Emőke u. 1/b, H-2030 Érd (HU). PAP, László [HU/HU]; Gyöngyvirág u. 23, H-2030 Érd (HU). SZÉKELY, István [HU/HU]; Krajcár u. 6, H-2110 Dunakeszi (HU). (74) Common Representative: CHINOIN GYÓGYSZER ÉS VEGYÉSZETI TERMÉKEK GYÁRA RT; Iparjogi Osztály, Tó u. 1-5, H-1045 Budapest (HU).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 3 July 1997 (03.07.97)	

(54) Title: PESTICIDE COMPOUNDS, COMPOSITIONS AND PROCESS FOR THE PREPARATION THEREOF



## (57) Abstract

The invention relates to compounds of general formula (1), their optically active isomers and salts wherein Ar = alicyclic, aromatic or one or more heteroatom containing heterocyclic moiety, optionally substituted by one or more alkoxy-, methylenedioxy-, alkyl-, halogen-, haloalkyl-, or nitro-group and/or condensed with a benzene ring; R<sup>1</sup>, R<sup>2</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, R<sup>3</sup>, R<sup>4</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, or R<sup>3</sup>, R<sup>4</sup> are together =O, Y = C, PO, or YR<sup>3</sup>R<sup>4</sup> together (a) group; X = -O-, -NR<sup>10</sup>-, R<sup>9</sup> = H, alkyl, phenyl, substituted phenyl; R<sup>10</sup> = H, alkyl; R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> are independently H, alkyl, alkenyl, haloalkyl, or Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(YR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X- form together a carboximide group; E = H, halogen, methyl; m = 0, 1, 2; n = 0, 1; o = 0, 1, 2; p = 0, 1, 2, with the proviso, that the sum of the atoms or groups of the -(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X-(CR<sup>5</sup>R<sup>6</sup>)<sub>o</sub>-(CR<sup>7</sup>R<sup>8</sup>)<sub>p</sub> bridge skeleton is 3 and the -C≡C-E skeleton forms with the atoms of the bridge a linear chain, consisting of 6 atoms ending preferably in a methyl group, furthermore with the proviso, that if Ar stands for a naphthyl group, Y means C-atom, X means O-atom, R<sup>3</sup> and R<sup>4</sup> together cannot mean =O. The compounds of general formula (1) according to the invention can be applied as active ingredients of pesticide, preferably arthropodicide compositions, and as synergists of other arthropodicide active ingredients.

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## PESTICIDE COMPOUNDS, COMPOSITIONS AND PROCESS FOR THE PREPARATION THEREOF

This invention relates to alkynyl pesticide compounds of the general formula I.,  
 pesticide compositions containing the active ingredients of general formula I.,  
 5 furthermore the pesticide synergists of general formula I., and synergized  
 pesticide compositions with known pesticide active ingredients, and the process  
 for the preparation thereof.

In general formula I the substituents have the following meanings:

10 Ar = an alicyclic-, aromatic-, or one or more heteroatom containing heterocyclic  
 moiety, optionally substituted by one or more alkoxy, methylenedioxy, alkyl,  
 halogen, haloalkyl or nitro group, and/or condensed with a benzene ring,

$R^1, R^2$  = independently hydrogen, alkyl, alkenyl, haloalkyl, phenyl, substituted  
 phenyl, cycloalkyl,

15  $R^3, R^4$  = independently hydrogen, alkyl, alkenyl, haloalkyl, phenyl, substituted  
 phenyl, cycloalkyl, or

$R^3, R^4$  are together =O;

Y = C, =PO, or

20  $YR^3R^4$  form together a  $\begin{array}{c} R^9 \\ | \\ -C=N- \end{array}$  group;

X = -O-; -NR<sup>10</sup>-;

R<sup>9</sup> = hydrogen, alkyl, phenyl, substituted phenyl;

R<sup>10</sup> = hydrogen, alkyl;

R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> are independently hydrogen, alkyl, alkenyl, haloalkyl, or

25 Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(YR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X- form together a carboximide group;

E = hydrogen, halogen, methyl;

m = 0, 1, 2;

n = 0, 1;

o = 0, 1, 2;

30 p = 0, 1, 2,

with the proviso that the sum of the atoms or groups of the bridge  $-(CR^1R^2)_m-(CR^3R^4)_n-X-(CR^5R^6)_o-(CR^7R^8)_p$  is 3 and the  $-C=C-E$  skeleton with the  
5 atoms of the bridge forms a linear chain, consisting of 6 atoms ending favorably in a methyl group.

furthermore with the proviso that if Ar is naphthyl group. Y means C-atom. X means O-atom.  $R^3$  and  $R^4$  together can not mean  $=O$ .

The invention includes furthermore the salts and the optically active isomers of  
10 the compounds of general formula I.

Narrower groups within compounds of general formula I. are represented by the compounds of general formula IA, IB, IC, ID, IE, IF, their salts and optically active isomers, where the meanings of the substituents are the same, as defined above.

15

Favourable representatives of the compounds of general formula I. are:

- 1-naphthyl-methyl 2-butyryl ether,
- 2-propynyl-1,3-benzodioxol-5-carboxylate,
- 1-[(2-butyryloxy)-ethyl]-3,4-dimethoxybenzene.
- 20 2,6-dichloro-1-(2-butyryloxymethyl)benzene.
- 1-[1-(2-butyryloxy)propyl]naphthalene.
- R-(+)-2-[1-(2-butyryloxy)ethyl]naphthalene.
- 5-[(but-2-ynyloxy)methyl]-1,3-benzodioxole.
- 5-[2-methyl-1-(2-butyryloxy)propyl]-1,3-benzodioxole.
- 25 5-[(but-2-ynyloxy)phenylmethyl]-1,3-benzodioxole.
- 2-[(2-butyryloxy)methyl]-1,4-benzodioxane.
- 2,3-dihydro-2,2-dimethyl-7-(3-pentyloxy)benzofuran

In the term Ar the aromatic group is favourably phenyl or naphthyl group.  
30 Ar as a heterocyclic moiety may contain one or more O, S, N heteroatoms, it may favourably represent benzodioxole-, benzodioxane-, 2-benzofuran-, 7-benzofuran-moieties.

The alicyclic group may favourably be condensed with a benzene ring, thus for instance may represent indane group, or 1,2,3,4-tetrahydronaphthyl group. The carboximide group may favourably represent phthalimide moiety.

5 The aromatic, heterocyclic and alicyclic Ar groups are optionally substituted by C<sub>1-4</sub> alkoxy-, methylenedioxy-, C<sub>1-4</sub> alkyl-, halogen-, C<sub>1-4</sub> haloalkyl- or nitro group.

Compounds which are non-toxic, or only slightly toxic alone, but given together with a pesticide, preferably arthropodicide agent they enhance markedly the  
10 potency of the latter, are called *synergists*. These materials may in principle act in several ways, however they exert their effect decisively by blocking the metabolism of the active substance. Metabolism may proceed via oxidative, hydrolytic, conjugative and absorption reactions and by the variations thereof. At present there is no unambiguous example for a synergist acting at the receptor  
15 level, neither do they play an important role in the praxis.

The synergistic potency e.g. in the case of insecticides is characterized by the so-called SR synergist ratio which is given as follows:

$$\text{SR}_{50} = \frac{\text{LD}_{50}\text{insecticide}}{\text{LD}_{50}\text{insecticide} + \text{synergist}}$$

20

The more the SR<sub>50</sub> value differs from 1, the higher is the synergistic potency. The use of synergists in arthropodicidal preparations is very attractive, since they afford a possibility to come out with new preparations with practically all  
25 representatives of the area. These new preparations, compared to the previous ones, promise to be less expensive, less toxic, more selective, encountering less environmental hazard, suppressing the evolution of resistance, and being active also on strains which already evolved resistance.

Following the discovery of synergists and the reveal of their mode of action, a  
30 wide-range research and development work started from the mid 60-ies till the late 70-ies to work out new synergists. This research, however resulted only a

few molecules which really attained application (at present the number of the registered insecticide synergists is less than 10). These compounds are of basic scientific importance in the research of resistance (K. F. Raffa and T. M. Priester, *J. Agric. Entomol.*, 2(1), 27-45, (1985)), however, there are only 2-3  
5 molecules listed as products in the Pesticide Manual, and only two materials (PBO, MGK264) which are actually on the market. The field application has been restricted by several factors: it is not easy to find a chemical tool which can be used selectively and safely, and the cost/effectiveness ratio of which is competitive with that of the active ingredient. To apply a synergist  
10 economically, it must be highly potent, it must act at small doses (not exceeding the original dose of the active ingredient).

On the basis of their chemical structures the presently known arthropodicide synergistic compounds may be divided into the following groups:

### 1.3-methylenedioxyphenyl (MDP) derivatives

15 ### O-2-propynyl and propynyl-homologues and their derivatives (ethers, oxim-ethers, esters)

### N-alkyl derivatives

### phosphor esters ...

### other derivatives e.g. thiocyanates, polyhalo ethers etc.

20 The compounds may also be divided into groups on the basis of their target of attack [K. F. Raffa and T. M. Priester, *J. Agric. Entomol.*, 2(1), 27-45, (1985)], but this grouping is rather theoretical, less exact, first of all because the actual metabolic processes are not fully known. The metabolism of most of the compounds proceeds consecutively, but may also proceed simultaneously, and  
25 may follow several mechanisms, thus the division is less informative, even if we consider the first step of the cascade degradation as the decisive step.

For the metabolic degradation of most arthropodicides first of all the oxygenase system is responsible. It is agreed in the literature that the compounds of this  
30 group exert their activity basically by blocking the cytochrome P-450 enzyme of the microsomal oxidation system [John E. Cassida, *J. Agr. Food Chem.*, 18(5),

- 753-772. (1970), R. M. Sacher, R. L. Metcalf and T. R. Fukuto: *J. Agr. Food Chem.*, **16**(5), 779-786. (1968)]. The enzymes forming the structurally analogous group of so-called isoenzymes constitute the major part of the detoxification system of the organisms [Ortiz de Montellano, P. R., Ed.
- 5 *Cytochrome P-450: Structure Mech. and Biochem.*, Plenum New York. (1986)]. They perform detoxification via mono-oxygenation of the substrate, producing a more polar product, which possibly after further transformations can be eliminated by the organism. The system degrades very different structures by the same way. Therefore they are also designated as Mixed Function Oxygenases
- 10 (MFO) and Polysubstrate Monooxygenases (PSMO).

On that basis one could expect that the surface of the enzyme is aspecific for the synergist, too. Quite the contrary, we have found that the compounds may be optimized.

- 15 For the isolation and testing of the Cytochrome P-450 enzymes of insects there are standard methods available [J. G. Scott and S. S. T. Lee: *Arch. Insect Biochem. and Phys.*, **24**, 1-19, (1993)]. The enzymes of various species may show great similarities, but they may also differ significantly from each other. The synergists known from the literature and investigated by us belong to the
- 20 group of O-2-propynyl, and propynyl-homologues and their derivatives (ethers, oxim-ethers, esters). As shown by the literature they exhibit different potency for the different species, which means that the oxidation capacity of the species varies to a certain extent. This is the reason for the high insect/mammal selectivity and synergist selectivity, characteristic for that group of compounds.
- 25 These selectivities, which cannot be directly explained by the above mode of action, are the bases of the development and safe application. On the other hand this is the reason why these compounds have not become commercially available. For all the compounds of the group prepared and evaluated so far we can tell, in general, that their effect was exclusively bound to the propynyl side-chain, this chain has been substituted in the allylic position by various aryl rings

mainly through an oxygen atom. The compounds known as yet may be divided into the following groups:

- ### Phenyl propargyl ethers [Fellig et. al., *J. Agr. Food Chem.*, 18(5), 78, (1970)]
- 5 ### Benzyl propargyl ethers [Ciba Geigy, *Ger. Offen.* 2 235 005 (1972)]
- ### Benzaldoxime propargyl ethers [Ciba Geigy, *Ger. Offen.* 2 016 190 (1970)]
- ### Naphthoic acid propargyl esters [Hoffman-La Roche, *Belg. Patent.* 867 849 (1978)]
- 10 ### Alkynylphthalimides [FMC, *Ger. Patent.* 1 217 693 (1966)]
- ### Phenylphosphonic acid propargyl esters [Niagara Chem. Div., FMC Corp., Technical Data Sheet on NIA 16824, (1968)]

- The first two groups are sub-divided into further groups owing to the high variability of the aromatic group and its substituents. Thus, there are known
- 15 naphthyl propargyl ethers [Hoffman-La Roche, *US* 3 362 871 (1968); Ciba Geigy, *Ger. Offen.* 2 100 325 (1971)],
- 4-hydroxyquinoline propargyl ethers [Alkaloida, *HU* 210 557, (1992)],
- methylenedioxybenzyl propargyl ethers [Sumitomo, *JP.* 03 01177, (1973)] and
- alpha-substituted methylenedioxybenzyl propargyl ethers [Sumitomo, *JP.*
- 20 61 24585, 61 24586 (1986)].

- In a study about naphthyl propynyl ethers it has been concluded that butynyl ethers, first of all 3-butynyl ethers are more potent than the analogous propargyl and pentynyl ethers [R. M. Sacher et. al., *J. Agr. Food Chem.*, 16, 779-786, (1968)]. Interestingly, however there was no continuation of that work, the
- 25 discovery has not been patented, either. Detailed analysis of the literature data suggest, that the propynyl side-chain cannot be replaced by homologous chains, since the publications and patents relate further on to propargyl derivatives.
- In order to clear this contraversion we have prepared the compounds in question, and found that in contrast to what was disclosed in the literature, the 2-
- 30 butynyl derivative (the one ending in a methyl group) is more potent than the 3-butynyl derivative; the alpha-isomers are more potent than the analogous beta-



isomers: and the 3-pentynyl derivative is more potent than the 2-butynyl derivative. These data suit well in our theory, and the data given in the literature might be the reason why this direction was not followed by others.

Similarly, there is a contraversion regarding the activity of the 4-

- 5 pentynylphthalimide derivatives: although they proved to be potent synergists of allethrin, they antagonized with pyrethrin [H. Jaffe, J. L. Neumeyer, *J. Med. Chem.*, 13, 901, (1970)]. In these structures again, the alkynyl chain ends in triple bond. The hybride variations of these structures, namely the N-alkyloxy-O-propargyl-phthalimides have also been prepared, here again the triple bond is  
10 in terminal position [Sumitomo, *NL*, 6 600 916 (1966)].

- To sum up, the most active representatives of the group, although on some tests exhibited outstanding activity, and were superior regarding their synergist/active ingredient ratio [D. J. Henessy, *Biochemical Toxicology of Insecticides*, Ed., R. D. O'Brian & I. Yamamoto, Academic Press, 105-114, (1970)], have never been  
15 applied in the praxis. This has several reasons: their activity did not reach the potency of earlier, well-established derivatives, they exhibited activity only in a narrow range, their potency was highly species-dependent, and within one species it depended greatly on the "strength" of the individual. Their safe and broad application was not therefore ensured.

- 20 The alkynyl compounds listed above are all derivatives of a common optimal structure, but the authors did not realize the relationships, and have not prepared the most active representatives, alloying and improving the advantages of these groups of compounds.

- We have experimentally tested, compared and analysed the biological effect of  
25 the known compounds, as well as that of the new derivatives prepared by us, and revealed the structural element which is responsible for the effect. On that basis we have prepared new compounds which surpass significantly the activity of the earlier ones and combine those properties which ensure effectiveness on more species and with more known active ingredients.

- 30 The integral part of the present invention is the discovery, that in the optimal compounds the carrier of the activity is a triple bond of an alkynyl structure with

an electron-rich Ar ring, which is connected to the triple bond through a mobile bridge consisting of three atoms. The atoms of the bridge are variable, and may have substituents, and so is the ring. To enhance the activity it is favourable to introduce lipophilic and electron-rich atoms and substituents. Thus the atoms of the bridge may be -besides of carbon atoms- oxygen, sulphur, nitrogen, and phosphor heteroatoms. These atoms may be linked through single or multiple bonds to each other and optionally with further substituents containing the above heteroatoms they may be substituted to further functional groups or derivatives. The atoms may be replaced by each other. The first element of the bridge may with its substituent form a ring, which may be attached to the aromatic ring, and thus may be part of the electron-rich moiety. Into the ring, linked to the bridge, heteroatoms, as listed above, may also be incorporated, and the effect may be further enhanced by the introduction of alkoxy, halogen, alkyl, haloalkyl or nitro substituents. The ring may be 5-, 6-, or 7-membered and may be condensed with a further ring, which is built according to the above principles, and may incorporate the first element of the bridge. Compounds in which the acetylenic hydrogen of the alkynyl side-chain is replaced by a methyl group exhibit higher activity than the the analogues with terminal triple bond. Keeping these rules we can carry out new substitutions by which we can modify the character of the compounds, according to the demand (lipophilicity, translaminarity, systemicity, etc.) of the application area.

Of the isomers of optically active compounds, e.g.  $\alpha$ -methyl-substituted benzyl derivatives, the R(+)enantiomers are more potent than the S(-)enantiomers. The difference between the activities of the isomers is growing with an enhancing activity of the racemic mixture.

The compounds developed by us are new, they are characterized by outstanding mammal/insect selectivity and high potency, exerted at low dose related to the active ingredient. This is attributed to the outstanding high receptor affinity of our compounds. In comparative experiments the indices of our compounds

highly surpassed those of earlier known synergists for active ingredients, whose metabolism is based on microsomal oxidation. This high activity and selectivity were also demonstrated in field studies conducted on small plots. The compounds did not show fito-toxicity, they did not separate from the active  
5 ingredients, their physico-chemical parameters fitted well with those of the active ingredient. Through these features the dose/efficacy/cost value, which earlier hindered the application, could favourably be modified and the application became possible.

With the active substances of general formula I the effect of the following  
10 known arthropodicide active ingredients may favourably be synergized:

Acetamide derivatives: e.g. oxamyl;

Benzoylurea compounds: e.g. flucycloxiuron, hexaflumuron, teflubenzuron, triflumuron;

Benzoylurea like IGR compounds;

15 Bicycloheptadien compounds: e.g. heptenophos;

Cross-bridged diphenyl compounds: e.g. etofenprox, bromopropylate, methoxychlor, temephos, tetradifon;

Carbamates: e.g. aminocarb, aldicarb, aldoxycarb, asulam, bendiocarb, benfuracarb, carbaryl, carbetamide, carbofuran, carbosulfan, diethofencarb,  
20 dioxacarb, ethiofencarb, fenobucarb, fenoxycarb, furathiocarb, isoprocarb, methomyl, oxamyl, pirimicarb (pirimor), propoxur, thiodicarb, thiofanox, xylylcarb;

Carbamoyloxime derivatives: e.g. alanycarb, butocarboxim;

Cyclodienes: e.g. aldrin, chlordane, endosulfan, heptachlor;

25 Diazoles: fipronil;

Hydrazides: RH 5992, RH 5849, CGA 215'944;

Nereistoxin analogues: pl. bensultap;

Nitroimidazolidynlenamines: e.g. imidacloprid;

Organophosphor compounds e.g. quinalphos, diazinon, phosalone, dimethoate,  
30 azinphos-methyl,

Organotin compounds e.g. azocyclotin, cyhexatin, fenbutatin oxide SSI-121;

- Phenoxy compounds: e.g. diafenthiuron:
- Pyrazoles: e.g. pyrazophos:
- Pyrethroides: e.g. allethrin, bioallethrin (esbol), acrinathrin, fenvalerate, empenethrin, prallethrin, resmethrin, MTI-800, flufenprox, permethrin,
- 5 tetramethrin, cypermethrin and their isomers and isomer-combinations:
- Pyridazinones: e.g. pyridaben:
- Pyridine derivatives: e.g. chlorpyrifos:
- Pyrimidine derivatives: e.g. pyrimiphos-ethyl, pyrimiphos-methyl:
- Pyrroles: e.g. AC 303-t, 630;
- 10 Quinazolines: e.g. fenazaquin:
- Terpenoid derivatives: e.g. methoprene:
- Tetrazines: e.g. clofentezine, SZI-121 (flufenzin):
- Thiadiazines: e.g. buprofezin:
- Thiazolidin: pl. hexythiazox;
- 15 Triazoles: pl. isazophos, RH 7988;
- Chlorinated hydrocarbons: lindane:
- Macrocyclic lactones;
- Tebufenpyrad;
- Fenpyroximate:
- 20 Triazamate:
- The above known active ingredients are described in the 8th and 10th Edition of the Pesticide Manual, European Patent Application No. 0635499 (SZI-121), A.G.Chem.New Compound review vol. 11(1993) and ACS Symposium Series 504 p. 272, respectively.
- 25 Compounds of the general formula I can be most preferably used to synergize the effect of carbamates preferably carbofuran.
- We have found that the compounds have dual action, they are superior synergists of arthropodicide active ingredients, and they also hinder the individual growth of arthropoda through an effect impeding the biosynthesis of
- 30 ecdison, a material, playing key role in the growth of arthropoda. There is thus an unambiguous relationship between the synergistic- and the individual

growth-hindering activities. This latter effect, beside the outstanding metabolism-blocking activity of the compounds, is also a consequence of the fact, that these materials, in contrast to the other, earlier known families of compounds, practically do not degrade, or degrade only extremely slowly in the organism of the arthropoda. Thus, when applied alone, at a long run, depending on the periods of the endocrin regulation, they are able to block the hormon synthesis and hinder the degradation of the endo and exo-biotica. Due to the toxins accumulating in the organism, the individuals become incapable of living, they do not eat, the production of eggs diminishes, and the reproduction stops.

Beside these enhanced activities, the toxicity values of the compounds on mammals did not increase. This can be attributed to the differences in the electrode potencial values of microsomal oxidation systems for mammals and for arthropoda. Whereas the oxidation potential values of the higher-order organisms are high, and therefore they are able to beat the electron-barrier of the complexed synergists, the oxidation system of the arthropoda, with its small potential, is not capable to oxidate, and by this to remove the complexed molecule from the surface of the enzyme, causing the paralysis of the system. This is the reason why the compounds can be applied safely and selectively. The over-average fast degradation and excretion of the compounds from mammalia, owing to their high enzyme activity and fast enzyme binding, ensure, in contrast to the arthropoda, that these materials do not enhance the effect of biotics found or taken up by the mammalian organism, and therefore they are safe.

The effect was demonstrated by us on various arthropode species. Applied alone, or as a synergist, the compounds were active on insects, plant-louses and also on acari. In the light of the above, this fact refers again to the qualitatively different detoxification system of the mammals.

A very valuable advantage of our compounds is that on applying them to species, which already evolved resistance, the toxic dose could be reduced below the original dose of the known active ingredient (measured on susceptible strains). This has not been experienced with other synergists. This makes

possible the safe and effective management of resistant populations, complying with the modern regulations.

Beside the expected advantages mentioned above (they make possible to develop tools which are less expensive, less toxic on mammals, selective, and  
5 can suppress resistance) with the help of these compounds a number of well-established active ingredients can be renewed, the market of which has fallen back in the past years, because resistance evolved against them. (Carbofuran, Quinalphos, Cartap, Methomyl). Our compounds create new application and market possibilities, since they enhance the potency of less active materials  
10 (Resmethrin, Bioallethrin, Pirimicarb etc.) to the level of the most active compounds, without increasing their toxicity. PBO, which is on the market in big lots, but -with natural resources running low- at increasing price, and which is drawing back because of its suspected tumor provoking effect, may also be replaced with the help of our compounds.

15

The preparation of the compounds of general formula I varies depending on the different groups of compounds, and can be carried out by the chemical methods, characteristic for the preparation of these groups.

Thus

20 a.) for the preparation of compounds of general formula IA, where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meaning as defined above, compounds of general formula II and III are reacted wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meaning as defined above, A and B are groups, suitable to form ester bond.

25

b.) for the preparation of compounds of general formula IB, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, Y, E, m, o, and p, have the same meaning as defined above.

30 compounds of general formula IV and V are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meaning as defined above, and C and D stand for groups, suitable to form amide bond.

- c.) for the preparation of compounds of general formula IC, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meaning as defined above. R<sup>3</sup> and R<sup>4</sup> independently mean H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl.
- 5 compounds of general formula VI and VII are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meaning as defined above. R<sup>3</sup> and R<sup>4</sup> may independently mean H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, F and G stand for groups, suitable to form ether bond,
- 10 d.) for the preparation of compounds of general formula ID, wherein Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>2</sup>R<sup>4</sup>)<sub>n</sub>-N- stands for caboximide group, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, o, and p, have the same meaning as defined above,  
the carboximide of general formula VIII is reacted with the compounds of general formula IX, wherein R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, o, and p, have the same  
15 meaning as defined above and Lg stands for a leaving group,
- e.) for the preparation of compounds of general formula IE, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, E, m, n, o, and p, have the same meaning as defined above,
- 20 compounds of general formula X and XI are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meaning as defined above.  
H and I stand for a group, suitable to form a
- $$\begin{array}{c} \text{-N-} \\ | \\ \text{R}^{10} \end{array}$$
- 25 group, wherein R<sup>10</sup>, has the same meaning as defined above,
- f.) for the preparation of compounds of general formula IF, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, o, and p, have the same meaning as defined above.  
compounds of general formula XII and IX are reacted, wherein Ar, R<sup>1</sup>, R<sup>2</sup>,  
30 R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, n, o, and p, have the same meaning as defined above,  
and Lg stands for a leaving group, and

if desired, the compound of general formula I can be transformed into its salts, or may be liberated from its salts and, if desired, the optically active isomers can be separated.

5

To prepare the compounds of general formula I advantageously:

a.) The acyl halide of general formula II is reacted with the alkynol of general formula III, or the carboxylic acid of general formula II is reacted with the alkynyl halogenide of general formula III, in the presence of an acid binding agent, or

10

the carboxylic acid of general formula II is reacted with the alkynol of general formula III in the presence of an activator, preferably diethyl azodicarboxylate and triphenylphosphine or dicyclohexylcarbodiimide and an acidic catalyst,

b.) The acyl halide of general formula II is reacted with the primary or secondary alkynylamine of general formula V, or the carboxamide of general formula IV is reacted with the alkynyl halogenide of general formula V, optionally in the presence of an acid-binding agent.

c.) The alcohol of general formula VI is reacted with the alkynyl halogenide of general formula VII, or the halogenide of general formula VI is reacted with the alkynol of general formula VII in the presence of a base, or the alcohol of general formula VI and the alkynol of general formula VII are reacted in the presence of an activator, preferably diethyl azodicarboxylate and triphenylphosphine or dicyclohexylcarbodiimide and an acidic catalyst.

25

d.) The carboximide of general formula VIII is reacted in the presence of a base with the alkynyl halogenide or -mesylate, -tosylate, -trifluoroacetate of general formula IX, or

30



e.) The secondary amine of general formula X is reacted with the alkynyl halogenide of general formula XI. or the halogenide of general formula X is reacted with the secondary amine of general formula XI in the presence of a base. or

5

f.) The aldoxime or ketoxime of general formula XII is reacted in the presence of a base with the alkynyl halogenide or -mesylate, -tosylate, -trifluoroacetate of general formula IX.

10 The compounds prepared and claimed by us are new. they are not disclosed in the literature. Their structures have been elucidated after purification. purity was checked by TLC and GC methods. The molecular formula of the compounds was proven by elementary analysis. and the structures were unequivocally supported by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR measurements.

15

The materials can be formulated as independent compositions or in admixture with other known arthropodicide active ingredients, and according to the application goal known carriers and other auxiliary materials may be used. Thus, by methods known per se. emulsion concentrates, microemulsions, dusts, aerosols, vaporators and smokers may be prepared. [Rhone Poulenc-Geronazzo: Surfactant and Specialities for Plant Protection. Application Manual (1994). ICI: Surfactants. Application Manual (1992)].

20

In the course of the application the preparation containing the compound of general formula I and the preparation containing the known active ingredients(s) can be used one after the other or by making a tank-mixture of them.

25

To demonstrate the scope of our invention we present the following examples. without limiting the scope to the examples.

30

Examples for preparation:

Purity of the compounds was checked by TLC and GC methods: (CP 9000, CP-SIL-5CB, 60 m x 0.53  $\mu$ m, 5 ml/min  $N_2$ , FID, 220°C). As shown by these  
5 methods all compounds had purity over 95%. Structure of the materials was supported by IR,  $^1H$  and  $^{13}C$ -NMR measurements, molecular formulae were proven by elementary analysis.

## 1. Alkynyl esters

## General procedure

## A.)

The appropriate alkynyl alcohole was dissolved in dry benzene, pyridine was  
15 added and the mixture was cooled to 0-5°C. To this mixture the acyl chloride was added at a rate that the inner temperature does not exceed 5°C. The reaction mixture was stirred at room temperature overnight, the precipitated pyridinium hydrochloride was filtered off. The filtrate was neutralized with hydrogen  
20 chloride solution, then washed subsequently with water and saturated sodium chloride solution, dried on  $MgSO_4$  and evaporated. The raw material was purified by chromatography.

## B.)

6 mmol of the acide were dissolved in 20 ml of dry THF and 1.0 g (6 mmol) of diethyl azodicarboxylate (DEAD) were added. The mixture was cooled on an  
25 ice-water bath, and the solution of 10 mmol of the alkynol and 1.6 g (6 mmol) of triphenylphosphine in 10 ml of THF was added. The characteristic orange colour of the DEAD gradually disappeared. The solution was stirred at room temperature overnight, then it was diluted with 50 ml of ethylacetate, washed with saturated sodium chloride solution, dried and evaporated. From the residue

the triphenylphosphine oxide crystallized on addition of hexane-ethylacetate mixture. The filtrate was purified by column chromatography.

	Compound	Mp(C <sup>0</sup> )	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
1.1 501	2-Propynyl 1,3-benzodioxol-5-carboxylate	69-70	3270, 3010, 2922, 2853, 2124, 1726, 1625, 1606, 1501, 1445, 1373, 1279, 1263, 1157, 1103, 1076, 1039, 762.	2.51 (1H, t, J=2.4 Hz, $\equiv$ C-H), 4.88 (2H, d, J=2.4 Hz, OCH <sub>2</sub> -C $\equiv$ ), 6.03 (2H, s, OCH <sub>2</sub> O), 6.83 (1H, d, J=8.2 Hz), 7.47 (1H, d, J=1.6 Hz), 7.66 (1H, dd, J=8.2, 1.6 Hz)	52.34 (OCH <sub>2</sub> -C $\equiv$ ), 74.92 ( $\equiv$ CH), 77.81 (OCH <sub>2</sub> -C $\equiv$ ), 101.85 (OCH <sub>2</sub> O), 107.99, 109.59 (C-4, C-7), 123.29 (C-5), 125.71 (C-6), 147.74 (C-3a), 151.91 (C-7a), 165.07 (CO ester)
1.2 502	2-Butynyl 1,3-benzodioxol-5-carboxylate	63-64	3016, 2959, 2920, 2244, 1714, 1626, 1606, 1508, 1450, 1372, 1276, 1240, 1163, 1117, 1078, 1036, 970, 925, 758.	1.86 (3H, t, J=2.3 Hz, $\equiv$ C-CH <sub>3</sub> ), 4.84 (2H, q, J=2.3 Hz, OCH <sub>2</sub> -C $\equiv$ ), 6.03 (2H, s, OCH <sub>2</sub> O), 6.83 (1H, d, J=8.2 Hz), 7.47 (1H, d, J=1.6 Hz), 7.67 (1H, dd, J=8.2, 1.6 Hz).	3.65 ( $\equiv$ C-CH <sub>3</sub> ), 53.19 (OCH <sub>2</sub> -C $\equiv$ ), 73.33 (OCH <sub>2</sub> -C $\equiv$ ), 83.17 ( $\equiv$ C-CH <sub>3</sub> ), 101.81 (OCH <sub>2</sub> O), 107.95, 109.62 (C-4, C-7), 123.69 (C-5), 125.62 (C-6), 147.72 (C-3a), 151.78 (C-7a), 165.33 (CO ester)

## 2. Alkynyl-amides

## General procedure

The solution of the acyl chloride was reacted with the solution of the alkynylamine, in the presence of pyridine, at room temperature. The suspension was diluted washed consecutively with water, diluted hydrochloric acid solution and sodium hydrocarbonate solution, dried, evaporated and purified by chromatography and crystallisation.

10	Compound	Mp(C°)	IR v(cm <sup>-1</sup> )	<sup>1</sup> H-NMR δ (ppm)	<sup>13</sup> C-NMR δ (ppm)
523	N-(2-butyryl)- 3,4-methylene- dioxy- benzamide	143-144	3334, 3075, 2918, 1641, 1620, 1605, 1546, 1500, 1485, 1313, 1264, 1239, 1042.	1.82 (3H, t, J=2.4 Hz, CH <sub>3</sub> -C≡), 4.16 (2H, m, NH-CH <sub>2</sub> -C≡), 6.02 (2H, s, (CH <sub>2</sub> O) <sub>2</sub> ), 6.23 (NH), 6.81 (1H, dd, J=0.6, 7.8 Hz, H-4), 7.28-7.34 (2H, m, H-6, H-7)	3.54 (CH <sub>3</sub> -C≡), 30.37 (NH-CH <sub>2</sub> -C≡), 74.72 and 79.77 (C≡C), 101.73 (OCH <sub>2</sub> O), 107.72, 108.02 (C-4, C-7), 121.70 (C-6), 128.26 (C- 5), 148.01 (C-3a), 150.49 (C-7a), 166.37 (CONH)
535	N-(2-Butyryl)- 2-naphthamide	133-134	3295 (NH), 3055, 2922, 2913, 2850, 1641, 1629, 1602, 1541, 1414, 1309, 776, 756	1.08 (3H, t, J=2.1 Hz, CH <sub>3</sub> -C≡), 3.38 (1H, s, NH), 4.10 (2H, m, CH <sub>2</sub> - C≡), 7.60 (2H, m), 8.0 (3H, m), 8.49 (1H, s, H- 1), 9.03 (1H, t, J=5.3 Hz)	3.27 (CH <sub>3</sub> -C≡), 29.11 (- CH <sub>2</sub> -C≡), 76.77 and 78.07 (C≡C), 124.29 (C- 3), 126.90, 127.82 (three signals overlapping), 128.08, 129.07, 131.51 (C-4a), 132.32 (C-2), 134.37 (C-8a), 166.07 (CO)

5	2.3 541	N-(2-Propynyl)- l-naphthamide	105-106	3229 (NH), 3046, 2963, 2927, 2118, , 1635, 1618, 1590, 1576, 1531, 1415, 1301, 1245, 1033, 788, 773, 759, 519	2.27 (3H, t, J=2.4 Hz, H- C≡), 4.24 (2H, q, J=2.4, CH <sub>2</sub> -C≡), 6.52 (1H, broad s, NH), 7.35 (1H, t, J=8.1 Hz), 7.50 (3H, m), 7.84 (2H, m), 8.26 (1H, m)	29.62 (-CH <sub>2</sub> -C≡), 71.80 (H-C≡C), 79.43 (H- C≡C), 124.59, 125.19, 125.29, 126.41, 127.14, 128.28, 130.06 (C-8a), 130.85 (C-2), 133.34 (C- 1), 133.59 (C-4a), 169.14 (CO)
10	2.4 542	N-(2-Butynyl)- l-naphthamide	120-122	3276 (NH), 3046, 3011, 2917, 2856, 1632, 1618, 1591, 1577, 1522, 1444, 1432, 1287, 1258, 783	1.83 (3H, t, J=2.1 Hz, CH <sub>3</sub> -C≡), 4.25 (2H, q, J=2.1 Hz, CH <sub>2</sub> -C≡), 6.25 (1H, s, NH), 7.31- 7.60 (3H, m), 7.85 (2H, m), 8.32 (1H, m)	3.50 (CH <sub>3</sub> -C≡), 30.24 (- CH <sub>2</sub> -C≡), 74.47 and 79.81 (C≡C), 124.59, 125.19, 124.62, 125.09, 125.37, 126.39, 127.10, 128.26, 130.11 (C-8a), 130.75 (C-2), 133.64 and 133.75 (C-1, C-4a), 169.03 (CO)
20						

### 3. Alkynylimides

#### General procedure

To the solution of phthalimide in dry DMF 1 molar equivalent of dry potassium carbonate was added and to this suspension was added dropwise the toluene solution of 1 molar equivalent of alkynyl bromide. The suspension was stirred at 80 °C for 3 hours, then it was poured on ice-water. the crystals were collected and crystallized from 96% ethanol.

	Compound	Mp(°C)	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
3.1 537	N-(But-2-ynyl)- phthalimide	216-218	3090, 3040 (H-C aromatic), 2957, 2920 (CH aliphatic), 2234 (C≡C) 1768, 1718 (CO), 1609 (C=C aromatic), 1468, 1431, 1397, 1354, 1333, 1126, 1090, 952, 775, 732, 712, 629, 560, 532.	1.76 (3H, t, J=2.3 Hz, CH <sub>3</sub> -C≡), 4.52 (2H, q, J=2.3 Hz, N-CH <sub>2</sub> -C≡), 7.86-7.91 (4H, m, aromatic)	3.12 (CH <sub>3</sub> -C≡), 27.16 (N-CH <sub>2</sub> -C≡), 73.82 (CH <sub>3</sub> -C≡), 79.06 (CH <sub>2</sub> - C≡), 123.48 (C-3, C-6), 131.64 (C-1, C-2), 134.87 (C-4, C-5), 167.01 (CO)

## 4. (Aryl-alkyl)-, alkyl-alkynyl ethers

## 4.0 Preparation of 1-[(2-butynyloxy)-ethyl]-3,4-dimethoxybenzene (compound 599)

In a 50 ml flask fitted with thermometer, magnetic stirrer, addition funnel, and connected to an inert gas system, the suspension of 30 ml of dry THF and 1.5 g (0.063 mol) of NaH (cca.90 %) was prepared. To the suspension was added dropwise, at room temperature the solution of 4.0 g (0.021 mol) of  $\alpha$ -methyl-veratryl alcohol in 21 ml of dry THF. The mixture was heated under reflux conditions for 1 hour, cooled to room temperature. 4.1 g (0.0315 mol) of 1-bromo-2-butyne were added, then the heating was continued. The reaction was followed by TLC (eluent: hexane-EtOAc 4:1). The reaction is completed in about 3-4 hours.

To the cooled thick suspension 50 ml of ether was added, the mixture was filtered on Celite, the filtrate was washed with distilled water, dried on magnesium sulfate and evaporated. The residual oil was purified by column chromatography (eluent: hexane-EtOAc 4:1,  $R_f=0.37$ ).

Yield: 2.3 g (9.8 mmol), 46.9 %.

Purity of the product was checked by GC analysis: (CP 9000, CP-SIL-5CB, 60 m x 0.53  $\mu$ m, 5 ml/min  $N_2$ , FID, 250°C)  $t_R = 12.0$  min. >99%

Proof of structure:

Elementary analysis: ( $C_{14}H_{17}O_3$ , 233.29):

calculated: C% 72.08, H% 7.35

found: C% 69.70, H% 7.21

IR ( $CHCl_3$ )  $\nu$   $cm^{-1}$ : 2976, 2855, 2837, 1605, 1595, 1514, 1465, 1419, 1371, 1353, 1311, 1260, 1164, 1141, 1086, 1027, 864

$^1H$ -NMR (200 MHz,  $CDCl_3$ )  $\delta$ :

1.46 (3H, d,  $J=6.5$ Hz,  $CH-CH_3$ ), 1.85 (3H, t,  $J=2.3$ Hz,  $\equiv C-CH_3$ ),

3.83 and 4.01 (2H, ABX<sub>3</sub>  $J_{AB}=15.0$ Hz,  $J_{AX}=J_{BX}=2.3$ Hz,  $\equiv C-CH_2O$ ),

3.87 and 3.89 (summa 6H, s each  $OCH_3$ )

4.55 (2H, q,  $J=6.5$  Hz, Ar-CHO),

6.80-6.89 (3H, m, aromatic).

$^{13}\text{C}$ -NMR (50 MHz,  $\text{CDCl}_3$ ) $\delta$ :

3.61 ( $\equiv\text{C}-\text{CH}_3$ ), 23.76 ( $\text{CH}-\text{CH}_3$ ), 55.87 ( $\text{OCH}_3$ ), 55.96 ( $\equiv\text{C}-\text{CH}_2\text{O}$ ).

75.36 ( $\equiv\text{C}-\text{CH}_2$ ), 76.40 ( $\text{Ar}-\text{CH}-\text{CH}_3$ ), 81.91 ( $\equiv\text{C}-\text{CH}_3$ ), 109.06 (C-2).

110.86 (C-5), 118.94 (C-6), 135.30 (C-1), 148.52 (C-3), 149.19 (C-4).

In an analogous way as described in Example 4.0 were prepared the following compounds:

	Compound	Mp( $^{\circ}\text{C}$ )	IR $\nu(\text{cm}^{-1})$	$^1\text{H}$ -NMR $\delta$ (ppm)	$^{13}\text{C}$ -NMR $\delta$ (ppm)
4.1 279	1-naphthyl- methyl 2-butyryl ether	oil	3044, 3001, 2945, 2920, 2854, 1598, 1509, 1356, 1166, 1086, 1067	1.93 (3H, t, $J=2.3$ Hz, $\text{C}\equiv\text{C}-\text{CH}_3$ ), 4.22 (2H, q, $J=2.1$ Hz, $\text{O}-\text{CH}_2-\text{C}\equiv\text{C}$ ), 5.06 (2H, s, $\text{C}_{10}\text{H}_7-$ $\text{CH}_2-\text{O}$ ), 7.45 (1H, t, $J=8$ Hz), 7.53 (3H, m), 7.84 (1H, d, $J=8.1$ Hz), 7.88 (3H, m), 7.88 (1H, d, $J=7.7$ Hz), 8.19 (1H, d, $J=8.2$ Hz)	3.6 ( $\text{C}\equiv\text{C}-\text{CH}_3$ ), 57.71 ( $\text{O}-\text{CH}_2-\text{C}\equiv\text{C}$ ), 69.72 $\text{C}_{10}\text{H}_7-\text{CH}_2-\text{O}$ ), 75.10 ( $\text{O}-\text{CH}_2-\text{C}\equiv\text{C}$ ), 82.76 ( $\text{O}-\text{CH}_2-\text{C}\equiv\text{C}$ ), 124.03, 125.10, 125.72, 126.19, 126.85, 128.43, 128.72, 131.79 (C-8a), 133.06, 133.70
4.2 292	1-[1-(2- butynyloxy)- ethyl]- naphthalene	oil	3052, 2977, 2921, 2856, 1596, 1509, 1444, 1371, 1095, 1078	1.67 (3H, d, $J=6.5$ Hz, $\text{CH}_3-\text{CH}$ ), 1.87 (3H, t, $J=2.3$ Hz, $\equiv\text{C}-\text{CH}_3$ ), 2.96 and 4.15 (summa 2H, ABX, $J_{\text{AB}}=15.0$ Hz, $J_{\text{AX}}=J_{\text{BX}}=2.3$ Hz, $\text{OCH}_2-\text{C}\equiv\text{C}$ ), 5.40 (1H, q, $J=6.5$ Hz, $\text{C}_{10}\text{H}_7-$ $\text{CH}-\text{O}$ ), 7.51 (3H, m), 7.61 (1H, d, $J=6.8$ Hz), 7.79 (1H, d, $J=8.1$ Hz), 7.89 (1H, dd, $J=7.9, 1.8$ Hz), 8.22 (1H, d, $J=8.1$ Hz)	3.64 ( $\text{C}\equiv\text{C}-\text{CH}_3$ ), 22.96 ( $\text{CH}_3-\text{CH}$ ), 56.37 ( $\text{O}-$ $\text{CH}_2-\text{C}\equiv\text{C}$ ), 74.29 ( $\text{CH}_3-$ $\text{CH}$ ), 75.36 and 82.14 ( $\text{C}\equiv\text{C}$ ), 123.26 (C-8), 123.52, 125.50, 125.85, 127.92, 128.83, 130.78 (C-8a), 133.88 (C-4a), 138.42 (C-1)



4.3 454	1-[1-(2-butynyloxy)-propyl]-naphthalene	oil	3058, 3048, 3000, 2962, 2932, 2923, 2876, 2856, 1598, 1509, 1460, 1105, 1062.	1.02 (3H, t, $J = 7.4$ Hz, $\text{CH}_3\text{-CH}_2$ ), 1.89 (3H, t, $J = 2.3$ Hz, $\text{C}\equiv\text{C-CH}_3$ ), 2.03 (2H, m, $\text{CH}_3\text{-CH}_2$ ), 3.95 and 4.17 (summa 2H, ABX, $J_{AB} = 15.0$ Hz, $J_{AX} = J_{BX} = 2.3$ Hz, $\text{OCH}_2\text{-C}\equiv\text{C}$ ), 5.15 (1H, t, $J = 6.4$ Hz, $\text{C}_{10}\text{H}_7\text{-CH-O}$ ), 7.53 (3H, m), 7.59 (1H, d), 7.81 (1H, d), 7.89 (3H, m), 8.27 (1H, d)	3.59 ( $\text{C}\equiv\text{C-CH}_3$ ), 10.62 ( $\text{CH}_3\text{-CH}_2$ ) 30.27 ( $\text{CH}_3\text{-CH}_2$ ), 56.54 ( $\text{O-CH}_2\text{-C}\equiv\text{C}$ ), 75.50 ( $\text{O-CH}_2\text{-C}\equiv\text{C}$ ), 80.08 and 81.96 ( $\text{OCH-naphthyl}$ and $\text{O-CH}_2\text{-C}\equiv\text{C}$ ), 123.43 (C-8), 124.40, 125.31, 125.36, 125.73, 127.91, 128.79, 131.19 (C-8a), 133.88 (C-4a), 137.12 (C-1)
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	Compound	Mp(C°)	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
4.4 472	1-[2-methyl-1-(2-butynyloxy)-propyl]-naphthalene	oil	3051, 2959, 2922, 2871, 1598, 1509, 1466, 1064.	0.87 and 1.16 (summa 6H, d each, $J = 6$ Hz, $\text{CH}(\text{CH}_3)_2$ ), 1.88 (3H, t, $J = 2.3$ Hz, $\text{C}\equiv\text{C-CH}_3$ ), 2.31 (1H, m, $\text{CH}(\text{CH}_3)_2$ ), 3.89 and 4.14 (2H summa ABX <sub>3</sub> , $J_{AB} = 15$ Hz, $J_{AX} = J_{BX} = 2.3$ Hz, $\text{OCH}_2$ ), 4.92 (1H, d, $J = 6$ Hz, $\text{CH-O}$ ), 7.53 (4H, m), 7.83 (1H, d, $J = 8$ Hz), 7.91 (1H, dd, $J = 7, 2$ Hz), 8.30 (1H, d, $J = 7.6$ Hz)	3.57 ( $\text{C}\equiv\text{C-CH}_3$ ), 19.87 and 18.77 ( $\text{CH}(\text{CH}_3)_2$ ), 34.20 ( $\text{CH}(\text{CH}_3)_2$ ), 56.71 ( $\text{OCH}_2$ ), 75.67 ( $\text{C}\equiv\text{C-CH}_3$ ), 81.77 ( $\text{C}\equiv\text{C-CH}_3$ ), 123.84 (C-8), 125.15, 125.31, 125.39, 125.60, 127.91 (C-4), 128.76 (C-5), 131.74 (C-8a), 133.87 (C-4a), 136.56 (C-1).

4.5 389	1-[(1-methyl-(2-propynyloxy)-methyl)-naphthalene]	oil	3306, 3049, 2990, 2935, 2866, 1599, 1510, 1447, 1374, 1327, 1099, 1064	1.51 (3H, d, J=6 Hz), CH <sub>3</sub> ; 2.56 (1H, d, J=2 Hz), CH; 4.30 (H, qxd J=6.2 Hz) OCH; 4.91 and 5.34 (2H, AB, J <sub>AB</sub> = 15 Hz) OCH <sub>2</sub> ; 7.46 (1H, dd, J=7.8 Hz), 7.54 (3H, m), 7.86 (2H, m), 8.18 (1H, mxd, J=6 Hz) aromatic	22.1, CH <sub>3</sub> , 64.25, OCH; 68.99, CH; 73.34, aryl-CH <sub>2</sub> ; 83.71, CH-C; 124.11, C-8; 125.17, C-2; 125.74, C-3; 126.18, C-6, 126.92, C-7; 128.47, C-4; 128.75, C-5; 131.88, C-8a, 133.20, C-4a; 133.77, C-1
4.6 256	2-[1-(2-propynyloxy)-ethyl]-naphthalene	oil	3307, 3000, 2979, 2929, 2857, 1603, 1505, 1442, 1373, 1311, 1270, 1215, 1087, 1055, 860, 821, 633	1.58 (3H, d, J= 6.5 Hz, CH <sub>3</sub> -CH), 2.44 (1H, t, J=2.4 Hz) CH, 3.92 (1H, dd, J=2.4, 15.7 Hz) OCH <sub>2</sub> -C≡C, 4.13 (1H, dd, J=2.4, 15.7 Hz), OCH <sub>2</sub> -C≡C, 4.84 (1H, q, J=6.5 Hz, C <sub>10</sub> H <sub>7</sub> -CH-O), 7.50 (3H, m), 7.77 (1H, s), 7.85 (3H, m)	23.66 (CH <sub>3</sub> -CH), 55.55 (O-CH <sub>2</sub> -C≡C), 74.07 and 76.80 (CH-O, CCH), 79.98, (CCH), 124.11, (C-6), 125.60 (C-7), 125.90, 126.15, 127.68, 127.85, 128.5, 133.16, 133.21, 139.75 (C-1)
4.7 293	2-[1-(2-butyryloxy)-ethyl]-naphthalene	oil	3051, 2977, 2920, 2854, 1602, 1444, 1084	1.57 (3H, d, J= 6.5 Hz, CH <sub>3</sub> -CH), 1.87 (3H, t, J=2.3 Hz, CH <sub>3</sub> -C), 3.90 and 4.08 (1-1H, ABX3, J=15, 2.3 Hz, OCH <sub>a,b</sub> -C≡C), 4.79 (1H, q, J=6.5, C <sub>10</sub> H <sub>7</sub> -CH-O), 7.49 (3H, m), 7.77 (1H, bs, H-1), 7.85 (3H, m)	3.64 (C≡C-CH <sub>3</sub> ), 23.78 (CH <sub>3</sub> -CH), 56.23 (O-CH <sub>2</sub> -C≡C), 75.28 (C≡C-CH <sub>3</sub> ), 76.72 (CH-CH <sub>3</sub> ), 82.10 (C≡C-CH <sub>3</sub> ), 124.14, (C-6), 125.42, 125.78, 126.05, 127.64, 127.80, 128.40, 133.07 (C-4), 133.19 (C-8), 140.14 (C-2)

	Compound	Mp(C <sup>0</sup> )	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
4.8 441	5-[(But-2-ynyloxy)-methyl]-1,3-benzodioxole	oil	2997, 2946, 2921, 2888, 2376, 1609, 1503, 1491, 1445, 1251, 1099, 1070, 1042, 937, 865, 810	1.87 (3H, t, J=2.3 Hz, Me), 4.10 (2H, q, J=2.3 Hz, O-CH <sub>2</sub> -C $\equiv$ ), 4.47, (2H, s, O-CH <sub>2</sub> -Ar), 5.94 (2H, s, O-CH <sub>2</sub> -O), 6.76 (1H, d, J=8 Hz, H-7), 6.81 (1H, dd, J=8.15 Hz, H-6), 6.86 (1H, J=1.5 Hz, H-4)	3.52 (Me), 57.29 (O-CH <sub>2</sub> -C $\equiv$ ), 71.15 (O-CH <sub>2</sub> -Ar), 82.54 (CH <sub>3</sub> -C $\equiv$ ), 100.9 C-2, 107.95, 108.71 (C-4,7), 121.66 (C-6), 131.39, (C-5), 147.15, 147.66 (C3a, C-7a)
4.9 484	5-[2-Methyl-1-(2-butynyloxy)-propyl]-1,3-benzodioxole	oil	2958, 2921, 2874, 1608, 1502, 1486, 1441, 1076, 1041, 940	0.63 and 0.94 (summa 6H, d each, J = 6.8 Hz, CH(CH <sub>3</sub> ) <sub>2</sub> ), 1.76 (3H, t, J = 2.3 Hz, C $\equiv$ -CH <sub>3</sub> ), 1.81 (1H, m, CH(CH <sub>3</sub> ) <sub>2</sub> ), 3.69 and 3.94 (summa 2H, ABX <sub>3</sub> , J <sub>AB</sub> =15.1 Hz, J <sub>AX</sub> = J <sub>BX</sub> = 2.3 Hz, OCH <sub>2</sub> ), 3.86 (1H, d, J = 7.8 Hz, CH-O), 5.87 (2H, AB, OCH <sub>2</sub> O), 6.62 (1H, dd, J = 7.9, 1.6 Hz, 6-H), 6.68 (1H, d, J = 7.9 Hz, 7-H), 6.71 (1H, d, J = 1.6 Hz, 4-H)	3.58 (C $\equiv$ -CH <sub>3</sub> ), 18.93 and 19.30 ((CH(CH <sub>3</sub> ) <sub>2</sub> ), 34.42 (CH(CH <sub>3</sub> ) <sub>2</sub> ), 56.20 (OCH <sub>2</sub> ), 75.48 (C $\equiv$ -CH <sub>3</sub> ), 81.66 (C $\equiv$ -CH <sub>3</sub> ), 86.25 (CH-O), 100.85 (OCH <sub>2</sub> O), 107.44, 107.63 (C-4, 7), 121.29 (C-6), 134.48 (C-5), 146.88 and 147.63 (C-3a, 7a)

4.10 554	5-[(But-2-ynoxy)-cyclohexyl-methyl]-1,3-benzodioxole	oil	2920, 2877, 2851, 1610, 1502, 1485, 1441, 1357, 1243, 1132, 1064, 1040, 942.	0.84-1.31 (6H, m), 1.50-1.77 (4H, m) 1.83 (3H, t, $J=2.3$ Hz, $\equiv$ C-CH <sub>3</sub> ), 2.08 (1H, m, H-1'), 3.76 and 4.01 (ABX <sub>3</sub> , $J_{AB}=15$ Hz, $J_{AX}=J_{BX}=2.3$ Hz, OCH <sub>2</sub> ), 3.98 (1H, d, $J=8.3$ Hz, CH-O), 5.97 (2H, s, OCH <sub>2</sub> O), 6.65-6.78 (3H, m).	3.64 (C $\equiv$ C-CH <sub>3</sub> ), 25.93 and 26.05 (C-2', C-6'), 26.52 (C-3), 29.25 and 29.86 (C-3', C-5'), 43.97 (C-1'), 56.19 (OCH <sub>2</sub> ), 75.57 (C $\equiv$ C-CH <sub>3</sub> ), 81.64 (C $\equiv$ C-CH <sub>3</sub> ), 85.45 (CH-O), 100.88 (OCH <sub>2</sub> O), 107.47 and 107.64 (C-4, C-7), 121.31 (C-6), 134.48 (C-5), 146.91 and 147.69 (C-3a, C-7a).
4.11 555	5-[(But-2-ynoxy)-phenyl-methyl]-1,3-benzodioxole	oil	2993, 2887, 2859, 1605, 1502, 1486, 1442, 1357, 1239, 1037, 937.	1.89 (3H, t, $J=2.3$ Hz, $\equiv$ C-CH <sub>3</sub> ), 4.12 (2H, q, $J=2.3$ Hz, OCH <sub>2</sub> ), 5.56 (1H, s, CH-O), 5.93 (2H, s, OCH <sub>2</sub> O), 6.74-6.86 (3H, m), 7.25-7.39 (5H, m)	3.69 (C $\equiv$ C-CH <sub>3</sub> ), 56.34 (OCH <sub>2</sub> ), 75.12 (C $\equiv$ C-CH <sub>3</sub> ), 81.23 (C $\equiv$ C-CH <sub>3</sub> ), 82.56 (CH-O), 100.99 (OCH <sub>2</sub> O), 107.78 and 107.95 (C-4, C-7), 120.98 (C-6), 127.01 (C-2', C-6'), 127.50 (C-4'), 128.36 (C-3', C-5'), 135.54 (C-5), 141.62 (C-1'), 147.05 and 147.83 (C-3a, C-7a)

	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR δ (ppm)	<sup>13</sup> C-NMR δ (ppm)
4.12 493	(2-Butynyloxy-methyl)-3,4-dimethoxy-benzene	oil	3025, 3000, 2956, 2937, 2921, 2855, 2839, 1607, 1595, 1512, 1466, 1443, 1420, 1158, 1140, 1070, 1028	1.84 (3H, t, J=2.3 Hz, C≡C-CH <sub>3</sub> ), 3.83 and 3.85 (summa 6H, CH <sub>3</sub> O), 4.08 (2H, q, J=2.3 Hz, OCH <sub>2</sub> C≡C-), 4.48 (2H, s, aryl-CH <sub>2</sub> ), 6.77-6.88 (3H, m, aryl)	3.45 (C≡C-CH <sub>3</sub> ), 55.67 and 55.71 (CH <sub>3</sub> O), 57.31 (OCH <sub>2</sub> C≡C-), 71.22 (aryl-CH <sub>2</sub> ), 75.0 (C≡C-CH <sub>3</sub> ), 82.42 (C≡C-CH <sub>3</sub> ), 110.76 (C-2), 111.23 (C-5), 120.54 (C-6), 130.05 (C-1), 148.58 (C-4), 148.88 (C-3).
4.13 503 —	2,6-Dichloro-1-(2-butynyloxy-methyl)-benzene	oil	2931, 2918, 2881, 2849, 2241, 1584, 1563, 1473, 1356, 1198, 1157, 1091, 1073, 787, 769	1.87 (3H, t, J=2.3 Hz, ≡C-CH <sub>3</sub> ), 4.21 (2H, q, J=2.3 Hz, OCH <sub>2</sub> C≡C-), 4.83 (2H, s, C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> -O-CH <sub>2</sub> ), 7.17 (1H, dd, J=9.1, 6.7 Hz), 7.31 (2H, m)	3.64 (≡C-CH <sub>3</sub> ), 58.68 (OCH <sub>2</sub> C≡C-), 66.15 (C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> -O-CH <sub>2</sub> ), 74.94 (OCH <sub>2</sub> C≡C-), 82.81 (≡C-CH <sub>3</sub> ), 128.33 (C-3, C-5), 129.96 (C-4), 133.17 (C-2, C-6), 136.97 (C-1)
4.14 498	1-(2-Butynyloxy)-1,2,3,4-tetrahydronaphthalene	oil	2998, 2941, 2860, 1604, 1489, 1440, 1070, 1044	1.84 (3H, t, J=2.3 Hz, C≡C-CH <sub>3</sub> ), 3.83 and 3.85 (summa 6H, CH <sub>3</sub> O), 4.08 (2H, q, J=2.3 Hz, OCH <sub>2</sub> C≡C-), 4.48 (2H, s, aryl-CH <sub>2</sub> ), 6.77-6.88 (3H, m, aryl)	3.45 (C≡C-CH <sub>3</sub> ), 55.67 and 55.71 (CH <sub>3</sub> O), 57.31 (OCH <sub>2</sub> C≡C-), 71.22 (aryl-CH <sub>2</sub> ), 75.0 (C≡C-CH <sub>3</sub> ), 82.42 (C≡C-CH <sub>3</sub> ), 110.76 (C-2), 111.23 (C-5), 120.54 (C-6), 130.05 (C-1), 148.58 (C-4), 148.88 (C-3)

4.15 479	1-(2- Butynyloxy)- indane	oil	3073, 3000, 2938, 2924, 2854, 2243, 1711, 1667, 1608, 1461, 1332, 1097, 1063, 1018	1.91 (3H, t, $J = 2.3$ Hz, $C \equiv C-CH_3$ ), 2.15 (1H, dddd, $J = 13.2, 8.4, 4.8,$ 3.8 Hz, 2-H), 2.37 (1H, dddd, $J = 15, 8.4, 6.5, 6.5$ Hz, 2-H), 2.83 (1H, ddd, $J = 15.8, 8.4, 4.8$ Hz, 3-H), 3.12 (1H, ddd, $J = 15, 7.2, 8.4, 3-$ H), 4.21 (2H, q, $J = 2.3$ Hz, $OCH_2$ ), 5.14 (1H, dd, $J = 6.5, 3.7$ Hz, 1-H), 7.23 (1H, m), 7.28 (2H, m), 7.45 (1H, d, $J = 7$ Hz).	3.52 ( $C \equiv C-CH_3$ ), 30.11 (C-2), 32.25 (C-3), 56.14 ( $OCH_2$ ), 75.45 ( $C \equiv C-CH_3$ ), 81.68 (C- 1), 82.15 ( $C \equiv C-CH_3$ ), 124.80, 125.16 (C-5,6), 126.11, 128.36 (C-4,7), 142.10, 144.14 (C- 3a,7a).
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	Compound	Mp(C <sup>0</sup> )	IR $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
5 10 15 20 25	4.16 510 2-[(2-Butynyloxy)-methyl]-1,4-benzodioxane	oil	2996, 2921, 2858, 2222, 1594, 1492, 1466, 1269, 1097, 1043	1.87 (3H, t, J=2.4 Hz, . 3.70 and 3.80 (2H, ABX, J <sub>AB</sub> =10.1 Hz, J <sub>AX</sub> =J <sub>BX</sub> =5.0 Hz, CH-CH <sub>2</sub> -O), 4.08 (1H, dd, J=7.6, 11.8 Hz, H-3 $\beta$ ), 4.20 (2H, d, J=2.3 Hz, O-CH <sub>2</sub> -C $\equiv$ ), 4.28-4.41 (2H, m, H-3 $\alpha$ , H-2 $\alpha$ ), 6.81-6.92 (4H, m, C <sub>6</sub> H <sub>4</sub> )	3.57 (H <sub>3</sub> C-C $\equiv$ ), 59.43 (O-CH <sub>2</sub> -C $\equiv$ ), 65.58 (CH-CH <sub>2</sub> -O), 68.12 (C-3), 71.96 (C-2), 74.54 (CH <sub>2</sub> -C $\equiv$ ), 83.22 (H <sub>3</sub> C-C $\equiv$ ), 117.12, 117.40 (C-5 and C-8), 121.37, 121.56 (C-6 and C-7), 143.07, 143.21 (C-4a, C-8a)
	4.17 539 2-(2-butynyloxy-methyl)-2,3-dihydro-benzofuran	oil	3598, 3478 (broad), 3080, 3040, 2996, 2952, 2871, 1611, 1598, 1481, 1462, 1232, 1092, 1050, 1012, 1004, 954, 899, 865	2.65 (1H, t, J=5.4 Hz, OH), 2.97 and 3.25 (summa 2H, ABX, J <sub>AB</sub> =15.6 Hz, J <sub>AX</sub> =9.4 Hz, J <sub>BX</sub> =7.5 Hz, H-3), 3.79 (2H, m, CH <sub>2</sub> -OH), 4.90 (1H, m, H-2), 6.79 (1H, d, J=8.0 Hz), 6.87 (1H, td, J=7.5, 0.8 Hz), 7.11 (1H, d, J=7.8 Hz), 7.16 (td, J=7.2, 0.5 Hz)	31.18 (C-3), 64.77 (CH <sub>2</sub> -OH), 83.02 (C-2), 109.36 (C-7), 120.54 (C-5), 124.97 (C-6), 126.48 (C-3a), 127.95 (C-4), 159.08 (C-7a)

	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	$[\alpha]_D^{20}$
5	4.18 330 S-(-)-1-[1-(2-butynyloxy)-ethyl]-naphthalene	oil	like 4.2 292	(-) 78° (c=1, MeOH)
	4.19 331 R-(+)-1-[1-(2-butynyloxy)-ethyl]-naphthalene	oil	like 4.2 292	(+) 155° (c=1, chloroform)
10	4.20 456 S-(-)-2-[1-(2-butynyloxy)-ethyl]-naphthalene	oil	like 4.7 293	(-) 190.8° (c=1.0, chloroform)
	4.21 455 R-(+)-2-[1-(2-butynyloxy)-ethyl]-naphthalene	oil	like 4.7 293	(+) 199.0° (c=1.17, chloroform)
15	4.22 474 S-(-)-2-[1-(2-propynyloxy)-ethyl]-naphthalene	oil	like 4.6 256	(-) 224.4° (c=1.18, chloroform)
20	4.23 475 R-(+)-2-[1-(2-propynyloxy)-ethyl]-naphthalene	28-29	like 4.6 256	(+) 228° (c=1, chloroform)



## 5. Aromatic alkyl-alkynyl-amine derivatives

## General procedure

The amine was dissolved in dry benzene, the alkynyl bromide was added and the mixture was stirred at room temperature. Then it was diluted with water and ether, the phases were separated, the aqueous phase was twice extracted with ether, the combined organic phases were washed with water, and dried on  $\text{MgSO}_4$ .

	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR $\delta$ (ppm)	<sup>13</sup> C-NMR $\delta$ (ppm)
5.1 251	N- $\alpha$ -dimethyl- N-2-propynyl- $\beta$ -naphthyl- methylamine	51-53	3173, 3053, 2970, 2941, 2837, 2788, 1600, 1444, 1433, 1371, 1334, 1295, 1227, 1123, 1074, 1011, 969, 952, 935, 900, 863, 827, 754, 734, 713, 557, 482	1.455 (3H, d, CH-Me), 2.271 (1H, s, CCH), 2.360 (3H, s, NMe), 3.253-3.302 and 3.487-3.530 (2H, CH <sub>2</sub> ), 3.708-3.757 (1H, m, CHMe), 7.260-7.834 (7H, m, aromatic)	

## 6. Aryl alkynyl ethers

## General procedure

## 5 A.)

The appropriate phenol was dissolved in dry DMF and to the solution dry  $K_2CO_3$  and the appropriate alkynyl halogenide were added. The reaction mixture was heated to  $60^\circ C$  and stirred at that temperature for 3-6 hours. DMF was then distilled off in vacuo, the residue was taken up in the mixture of  
10 chloroform and distilled water. The phases were separated, the aqueous phase was twice extracted with chloroform, the combined organic phases were washed consecutively with water and saturated sodium chloride solution, dried on  $MgSO_4$  and evaporated. The raw product was purified by chromatography.

## 15 B.)

$Ph_3P$  was dissolved in dry benzene in an inert atmosphere and to the solution the appropriate alcohol and then the phenol were added. The mixture was cooled to  $0-10^\circ C$ , and DEAD (diethyl-azo-dicarboxylate) was added slowly, in small portions, keeping the temperature below  $10^\circ C$ . The reaction mixture was  
20 stirred for 10-24 hours.

Work-up: the precipitated  $Ph_3PO$  was filtered off, the filtrate was washed with water, dried and evaporated. The residue was chromatographed.

## 25 C.)

0.01 mol of phenol were dissolved in 7 ml of dry acetonitrile and under argon atmosphere it was cooled to  $-4^\circ C$ . To the solution were then added 1.968g (0.0129 mol) DBU, keeping the temperature below  $-4^\circ C$ . To the resulting solution 1.8g copper(II)-chloride were added and parallelly the trifluoroacetate  
30 of the other reactant was prepared.

0.0115 mol alkynyl-alcohol were dissolved in 7 ml of acetonitrile, and the solution was cooled to -5 °C, under argon atmosphere. To the solution were added 1.968g (0.0129 mol) DBU, while keeping the temperature below -5 °C. To the mixture were added dropwise 1.6g (0.0115mol) trifluoroacetic  
5 anhydride, keeping the temperature below 2 °C. The resulting mixture was stirred at 0 °C for 30 mins.

The trifluoroacetate solution thus obtained was added dropwise to the first solution, keeping the temperature below 0 °C and the mixture was stirred at 0 °C for 5 hours. The reaction was followed by TLC. At the end of the reaction  
10 the acetonitrile was distilled off in vacuo. The residue was shaken with the mixture of 150 ml of benzene and 50 ml of water. The organic layer was washed consecutively with 1N hydrochloric acid, 1N sodium hydroxide, water and saturated sodium chloride solution, then dried and evaporated. The product was purified by chromatography.

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	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR δ (ppm)	<sup>13</sup> C-NMR δ (ppm)
5	6.1 547 1-(3-butynyloxy)- 4-nitro-benzene	92-94	3287, 3111, 3085, 3075, 2964, 2947, 2920, 1609, 1596, 1510, 1466, 1344, 1333, 1263, 1179, 1110, 1019, 856, 846, 753, 669, 653.	2.07 (1H, t, J=2.6 Hz, C≡C-H), 2.73 (2H, td, J=6.8, 2.6 Hz, CH <sub>2</sub> C≡C), 4.18 (2H, t, J=6.8 Hz, OCH <sub>2</sub> ), 6.97 and 8.18 (summa 4H, dm, J=9 Hz, C <sub>6</sub> H <sub>4</sub> )	19.37 (C≡C-CH <sub>2</sub> ), 66.60 (C≡C-H), 70.38 (OCH <sub>2</sub> ), 79.62 (C≡CH), 114.51 (C-2, C-6), 125.89 (C-3, C-5), 141.73 (C-4), 163.40 (C-1)
10	6.2 540 1-(3-pentynyloxy)-4- nitro-benzene	77-78	3067, 3048, 2963, 2917, 2886, 1923, 1607, 1594, 1512, 1467, 1403, 1339, 1260, 1178, 1110, 866, 856, 753, 694, 648, 628, 522, 506.	1.78 (3H, t, J=2.3 Hz, C≡C-CH <sub>3</sub> ), 2.66 (2H, m, CH <sub>2</sub> C≡C), 4.12 (2H, t, J=7.0 Hz, OCH <sub>2</sub> ), 6.95 and 8.18 (summa 4H, dm, J=9 Hz, C <sub>6</sub> H <sub>4</sub> )	3.57 (C≡C-CH <sub>3</sub> ), 19.61 (C≡C-CH <sub>2</sub> ), 67.26 (OCH <sub>2</sub> ), 74.27 (C≡C- CH <sub>3</sub> ), 77.84 (C≡C- CH <sub>3</sub> ), 114.49 (C-2, C- 6), 125.85 (C-3, C-5), 141.59 (C-4), 163.59 (C-1).
20	6.3 377 2,3-dihydro, 2,2- dimethyl-7-(3- butynyloxy)- benzofuran	78-80	3277, 3071, 3043, 2970, 2923, 2889, 2858, 2119, 2022, 1874, 1795, 1714, 1656, 1624, 1611, 1591, 1492, 1470, 1440, 1492, 1396, 1385, 1371, 1302, 1283, 1244, 1201, 1172, 1128, 1077, 999, 972, 946, 887, 838, 780, 753, 720, 682, 663, 635, 600, 546, 502, 458	1.512 (6H, s, diMe), 2.033 (1H, t, CH), 2.710 (2H, m, -CH <sub>2</sub> C), 3.027 (2H, s, CH <sub>2</sub> -ar), 4.206 (2H, t, O-CH <sub>2</sub> ), 6.739-6.815 (3H, m, aromatic)	19.12 (CH <sub>2</sub> -C), 27.88 (diMe), 42.93 (C-3), 66.79 (C-2), 69.61 (O- CH <sub>2</sub> ), 79.96 (CCH), 87.06 (CC), 113.31 (C- 6), 117.86 (C-5), 119.99 (C-4), 128.36 (C-9), 142.62 (C-7), 147.52 (C-8)
25					
30					

6.4 418	2,3-dihydro- 2,2- dimethyl-7-(3- pentynyloxy)- benzofuran	58-59.5	2977, 2963, 2942, 2918, 2880, 2849, 1621, 1591, 1492, 1468, 1389, 1369, 1329, 1305, 1286, 1245, 1203, 1174, 1135, 1115, 1080, 1065, 966, 947, 881, 860, 841, 779, 751, 718, 634, 598, 532, 499.	1.510 (6H, s, diMe), 1.800 (3H, t, Me), 2.627-2.672 (2H, m, - CH <sub>2</sub> C), 3.023 (2H, s, CH <sub>2</sub> -ar), 4.150 (2H, t, O-CH <sub>2</sub> ), 6.751-6.784 (3H, m, aromatic)	3.471 (Me), 19.63 (CH <sub>2</sub> -C), 28.18 (diMe), 43.26 (C-3), 67.54 (C- 2), 74.82 (CC-Me), 77.32 (O-CH <sub>2</sub> ), 87.26 (CC), 113.21 (C-6), 117.87 (C-5), 120.25 (C-4), 128.48 (C-9), 143.12 (C-7), 145.00 (C-8)
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## 7. Alkynyl-oxim-ethers

## General procedure

The oxime was transformed to the oxim-ether in the classical way, by reacting it with the alkynyl bromide in dimethyl formamide, in the presence of potassium carbonate (See method A under the preparation of naphthyl ethers). The raw product was in each case purified by coloumn chromatography.

	Compound	Mp(C°)	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR δ (ppm)	<sup>13</sup> C-NMR δ (ppm)
7.1 571	1-Aceto-naphthon-oxim-(2-butyryl)-ether	oil	2990, 2919, 2853, 2230, 1604, 1591, 1459, 1436, 1363, 1353, 1309, 1252, 1034, 1017, 1002, 912	1.94 (3H, t, J=2.3 Hz, CH <sub>3</sub> -C≡), 2.41 (3H, s, CH <sub>3</sub> -C=N), 4.84 (2H, q, J=2.3 Hz, O-CH <sub>2</sub> ), 7.46-7.57 (4H, m), 7.87 (2H, m), 8.15 (1H, m)	3.80 (CH <sub>3</sub> -C≡), 17.51 (CH <sub>3</sub> -C=N), 62.25 (O-CH <sub>2</sub> ), 75.33 (CH <sub>2</sub> -C≡), 82.75 (CH <sub>3</sub> -C≡), 125.15, 125.46 (C-6, C-7), 125.96 (C-3), 126.01 (C-3), 126.49 (C-2), 128.40 (C-5), 129.10 (C-4), 130.85 (C-1), 133.86 (C-4a), 135.27 (C-8a), 157.41 (CH <sub>3</sub> -C=N)
7.2 572	3,4-Dimethoxy-acetophenonoxym-(2-butyryl)-ether	85	3080, 3003, 2963, 2929, 2869, 2840, 2237, 1595, 1577, 1518, 1447, 1417, 1337, 1311, 1278, 1249, 1234, 1176, 1153, 1030, 937, 879, 804, 768, 634, 621	1.87 (3H, t, J=2.3 Hz, CH <sub>3</sub> -C≡), 2.23 (3H, s, CH <sub>3</sub> -C=N), 3.88 and 3.90 (CH <sub>3</sub> O), 4.75 (2H, q, J=2.3 Hz, O-CH <sub>2</sub> ), 6.83 (1H, d, J=8.4 Hz), 7.15 (1H, dd, J=8.4, 2 Hz), 7.29 (1H, d, J=2 Hz)	3.77 (CH <sub>3</sub> -C≡), 12.76 (CH <sub>3</sub> -C=N), 55.86 (CH <sub>3</sub> O), 62.23 (O-CH <sub>2</sub> ), 75.27 (CH <sub>2</sub> -C≡), 82.53 (CH <sub>3</sub> -C≡), 108.8 (C-5), 110.51 (C-2), 119.28 (C-6), 129.18 (C-1), 148.78 (C-3), 150.14 (C-4), 155.0 (CH <sub>3</sub> -C=N)

Activity results:Example 1.

Investigation of synergistic activity on house fly (*Musca domestica*) following topical application

In two parallel experiments 10 female, 2-4 day old house flies were treated on the ventral side of their thorax with 0.2  $\mu$ l of the test solution, with the help of Hamilton MicroLab P microdispenser. Beside *fixed synergist dose of 1000 ng/fly* the animals were treated with carbofuran at a dose of 20 ng/fly. For solvent cellosolve was used. Selection and counting of the flies were performed under the action of CO<sub>2</sub>. After treatment the flies were kept in plastic cups covered with tulle. Mortality after 24 hours was expressed in %. Results are demonstrated in the table below:

Material	Carbofuran+synergist (ng/fly)	
	20+0	20-1000
	mortality %	
<i>Alkynyl esters, amides, imides</i>		
501	3	53
502	0	47
523	0	17
535	3	27
541	0	46
542	0	42
<i>Aryl- alkyl- alkynyl ethers</i>		
279	0	72
256	0	32
441	1	97
484	0	63
493	1	100
599	10	100
503	0	95
292	0	72
293	0	45

5	454	0	75
	472	1	68
	479	1	58
	330	0	62
	331	0	72
	455	0	70
	456	0	47
	389	2	27
	554	0	58
10	555	0	90
	539	0	48
	474	0	50
	510	2	75
	498	5	70
15	475	0	47
Aromatic alkyl- alkyl-alkynyl- amine derivatives			
	251	2	37
Aryl alkynyl ethers			
	547	0	47
20	540	0	60
	377	0	57
	418	0	63
Aralkyl-aldoxime, ketoxime-alkynyl ethers			
	571	0	53
25	572	0	55

Example 2.

Investigation of synergistic activity on cotton bollworm (*Helicoverpa armigera*) following topical application

Treatment was performed similarly as described in Example 1. but L2 stadium grubs of cotton bollworms (*Helicoverpa armigera*) were treated as test animals. From the 24 hour dose - mortality data the LD<sub>50</sub> (ng/grub) values were



determined using probit analysis. None of the synergists acted at the applied 1000 ng/grub dose. Synergist ratio was calculated as the quotient of the LD50 values of carbofuran administered alone, and with the synergist. The experiments were performed in 2-4 replica. Synergist ratios are demonstrated in the table below:

	Materials	Synergist ratio
10	<i>Alkynyl-esters, amides</i> 501, 502, 523, 535, 541, 542, 537	>5
	<i>Aryl-alkyl alkyl-alkynyl ethers</i> 279, 256, 441, 484, 493, 503, 292, 293, 454, 510, 475, 498, 479, 472, 331, 455, 456, 389, 554, 555, 539, 474, 330, 599	>5
15	<i>Aromatic alkyl- alkyl-alkynyl-amine derivatives</i> 251	>5
	<i>Aryl alkynyl ethers</i> 540, 377, 418	>5
20	<i>Alkynyl-oximethers</i> 571 572	>5

### Example 3.

Investigation of synergist spectrum on house fly (*Musca domestica*) and cotton bollworm (*Helicoverpa armigera*) following topical administration

Synergistic activities of materials No. 279 and 599 of the present invention for various active ingredients were determined on house fly (*Musca domestica*) and cotton bollworm (*Helicoverpa armigera*) using methods of treatments as described in biological Examples 1 and 2. For the active ingredients ISO

common names are given (see: Pesticide Manual 1994). The obtained synergist ratios are shown below:

active ingredient	279		599	
	Musca domestica	Helicoverpa armigera	Musca domestica	Helicoverpa armigera
	Synergist ratio		Synergist ratio	
carbofuran	>20	>10	>40	>20
bendiocarb	>20	>10	>40	>20
isoprocarb	>40	-	>40	>20
fenobucarb	>10	-	>20	-
aminocarb	>20	-	>20	-
thiodicarb	>10	-	>10	-
methomyl	>10	-	>10	-
pirimicarb	>20	-	>20	-
dioxacarb	>20	-	>40	>20
propoxur	>20	>10	>40	>20
imidacloprid	>5	-	>5	-
lindan	>5	>5	-	-
azinphosmethyl	>5	>5	-	-
chlorpyrifos	>5	>5	-	-
esbiol	>5	-	>10	-
permethrin			>5	>10
tetramethrin			>5	-

Example 4.

Effect of the active ingredient:synergist ratio on the synergistic activity

Treatment was performed as described in Example 1. using Hamilton MicroLab P microdispenser. In two parallel experiments 10 female, 2-3 day old flies were treated on the ventral side of their thorax with 0.2  $\mu$ l test solution. Beside 1000-400-200-80 ng/fly fixed doses of the synergist they were treated with *constant* 20 ng/fly carbofuran. Selection and counting of the flies were performed under the action of CO<sub>2</sub>. After treatment the flies were kept in plastic cups covered with tulle. After 24 hours mortality % was recorded. Depending on the results the experiments were performed in 2-4 replica. Results are demonstrated in the table below.

Materials	Dose of the Synergist (ng/fly)				
	0	80	200	400	1000
	24 hour mortality (%)				
501	0	60	75	80	80
441	0	62	67	90	95
493	0	75	88	94	100
503	0	37	50	65	93
454	0	40	45	60	75
455	0	25	48	63	77
599	0	65	90	95	100

Example 5.

Investigation of synergistic activity on resistant house fly (*Musca domestica*) populations

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The table below demonstrates synergistic activities of materials of the present invention for various active ingredients on two resistant house fly strains (INSEL, IX). Investigation was carried out as described in biological Example 1. LD<sub>50</sub> values and synergist ratios were determined as given in Example 2.

10

Treatment	INSEL strain		IX strain	
	LD50 (ng/fly)	SR	LD50 (ng/fly)	SR
carbofuran	15375		>100000	
+ 279	29	530	94	4760
methomyl	475		851	
+ 279	46	10	109	5
pirimicarb	>100000		>100000	
+ 279	696	145	3562	115
aldicarb	695		2104	
+ 279	172	4	507	4
bendiocarb	100000		100000	
+ 279	150	667	746	134
isoprocarb	>100000		>100000	
+ 279	983	102	2145	47
esbiol	10653		-	
+ 279	794	13	-	-

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Example 6.

Investigation of synergistic activity on oat aphid (*Rhopalosiphum padi*)

5-8 cm high oat plants, sawn in plastic cups were infected with different aged specimens of *Rhopalosiphum padi* aphids. The settled aphids were counted before the treatment, then the plants were sprayed, using a hand sprayer, with 1 ml of the spray solution, beside the *administration of fixed dose (30 ppm) of the synergist*. Of compound No. 279 of the present invention a 100 g/l concentration emulgeable concentrate was prepared, by methods usual in the formulation praxis, applying solvent and surface active materials. Test solutions used for the spraying were prepared from this concentrate and from marketed preparations by dilution. Mortality of the aphids was determined 24 hours after the treatment. Results are shown below:

Treatment	Mortality %
carbofuran 1 ppm	<.50
carbofuran 1 ppm + 279	> 95
pirimor 2 ppm	< 30
pirimor 2 ppm + 279	> 95
imidacloprid 0.1 ppm	< 50
imidacloprid 0.1 ppm - 279	> 95

Example 7.

Investigation of the effect on fecundity, on house fly (*Musca domestica*)

Groups consisting of freshly hatched 50 male and 50 female flies were fed during 48 hours with granulated sugar comprising 500 ppm of material No. 441 and 484 of the present invention respectively, and the eggs layed on the next 10 days were raised. The fecundity-hindering effect was expressed as the quotient

of the emerged flies in the treated and untreated groups. The experiments were performed in 4 replica.

Treatment	Hindering effect on fecundity
441	87 %
484	90 %

### Example 8.

Synergism of acaricidal effect investigated on two-spotted spider mite (*Tetranychus urticae*)

From the first pair of leaves of a 1 week old bean plant leaf-discs of 225 mm diameter were cut which were treated by dipping them (5 min) into the test solution consisting of the active ingredient and the synergist in definite concentrations. For the preparation of the stock solutions of required concentration, 10 % acetone as co-solvent and 0.1 % Tween-80 as detergent were applied. The dried leaf-discs were placed on wet surface and they were infected with 10 grown-up female mites per leaf. After 48 hours the mortality was recorded using microscope and a brush. The experiment was performed in 4 replica. Averages of the results are shown in the table below.

Treatment with the active ingredients alone	Concentration (ppm)				
	31	62	125	250	500
	Mortality %				
279	0	6	8	18	30
carbofuran	13	39	44	81	90
bromopropylate	18	28	90	-	-
Treatment with the active ingredients in combinations	Concentration (ppm)				
	16+16	31+31	62+62	125+125	250+250
	Mortality %				
279+carbofuran	29	80	80	100	100
279+bromopropylate	75	90	100	-	-

Example 9.

Efficacy in field trial against Colorado potato beetle (*Leptinotarsa decemlineata*)

Of compound No. 279 of the present invention a 100 g/l concentration emulgeable concentrate was prepared by methods usual in the formulation praxis, applying solvent and surface active materials. Chinufur 40 FW composition, comprising 400 g/l carbofuran was applied together with a fixed dose of 2 l/ha of compound No. 279, in a small plot field study against Colorado potato beetle (*Leptinotarsa decemlineata*). Spraying was carried out with motoric sprayer (Maruyama) applying 300 l/ha spray solution. Treatments were performed in 4 replica, on plots of 25 m<sup>2</sup>. The effect of the treatments was evaluated on the 2nd day by counting the surviving beetles on the plants. Results are shown in the table below:

Treatment	Dose (l/acre)	carbofuran:279 ratio	Number of potato beetles piece/plant	
			before treatment	after treatment
untreated	-	-	23.6	28.0
Chinufur 40 FW	0.1	1:0	18.4	6.1
Chinufur 40 FW	0.2	1:0	32.0	6.8
Chinufur 40 FW+279	0.1+2.0	1:5	21.3	0.4

Example 10.

## Synergist activity of compound Nr. 599

Synergist activity of compound 599 with various specific acaricides was investigated against two-spotted spider mite (*Tetranychus urticae*), by the method described in Example 8. The  $LC_{50}$  and  $LC_{95}$  values calculated from the concentration-mortality relationship are shown in the table below.

Synergist activity against two-spotted spider mite (*Tetranychus urticae*)

Treatment	Ratio of Acaricide/ Synergist	Exposure time (h)	$LC_{50}$	$LC_{95}$	Synergist ratio	
			(mg)	( $\mu$ l)	$SR_{50}$	$SR_{95}$
Carbofuran	1:0	24	163.9	799.9	-	-
Carbofuran+MB-599	1:1	24	55.5	286.8	3.0	2.8
	1:2	24	33.5	93.7	4.9	8.5
	1:4	24	27.5	67.0	6.0	11.9
Fenazaquin	1:0	3	>1000	-	-	-
	1:0	24	41.9	801.3	-	-
Fenazaquin + PBO	1:1	3	326.7	>1000	>3.1	-
	1:1	24	20.4	371.8	2.1	2.2
Fenazaquin+MB-599	1:1	3	68.1	280.2	>15	-
	1:1	24	31.3	174.8	1.3	4.6
Tebuufenpyrad	1:0	3	>1000	-	-	-
	1:0	24	63.4	>1000	-	-
Tebuufenpyrad +PBO	1:1	3	115.9	1081	>9	-
	1:1	24	35.7	118.0	1.8	>8.5
Tebuufenpyrad+MB599	1:1	3	61.8	658.7	>16	-
	1:1	24	22.3	141.8	2.8	>7.0



Example 11.

Synergist activity against pea aphid (*Acyrtosiphon pisum*)

Synergist activity of compound No. 599 was tested against pea aphid (*Acyrtosiphon pisum*) in field trials on small plots (10 m<sup>2</sup>). 300 l/ha spray volume was applied using motoric sprayer (Maruyama). Efficacy was expressed by the average number of aphids/leaf before, and two days after the treatment, respectively. (Henderson and Tilton: J. Econ. Entomol., 48:157, 1955). Results are shown in the table below.

Treatment	Dose act. ingr./ha.	E (%)
Pirimicarb	250	93.8
	80	86.3
Pirimicarb + MB-599	80+80	95.5
Fipronil	240	94.6
Fipronil + MB-599	120+120	95.7
Carbofuran	160	99.1
	110	98.0
Carbofuran + MB-599	110+110	100.0
Triazamate	50	96.8
Triazamate + MB-599	33+33	97.7
Imidacloprid	120	98.4
Imidacloprid+MB-599	120+120	100.0

Example 12.

Comparative investigations with known reference synergists

LD<sub>50</sub> values of the reference compounds were determined in 4 replica on flies treated with carbofuran and 1000 ng of the known synergist, and the SR<sub>50</sub> ratios were counted in relation to the control carbofuran. These SR<sub>50</sub> ratios were

compared to those of the new compounds prepared by us. Our compounds were more active in each case.

1. Alkynyl esters

known

according to the  
invention

Synergist ratio	2-propynyl 1-naphthyl-carboxylate	502
SR <sub>50</sub>	4.11	6.28

2. (Aryl-alkyl), alkyl-alkynyl ethers

known

according to the  
invention

Synergist ratio	(2,6-dichlorophenyl)methyl 2-propynyl ether	503
SR <sub>50</sub>	20.92	21.16

known

according to the  
invention

Synergist ratio	5-[(2-propynyl)-methyl]-1,3-benzodioxole	441
SR <sub>50</sub>	10.60	25.70

known

according to the  
invention

Synergist ratio	1-naphthylmethyl 2-propynyl ether	279
SR <sub>50</sub>	5.28	28.7

known

according to the  
invention

Synergist ratio	2-[(2-propynyloxy)methyl]-1,4-benzodioxane	510
SR <sub>50</sub>	5.58	18.32

known

according to the  
invention

Synergist ratio	(2-propynyloxy-methyl)-3,4-dimethoxy-benzene	493
SR <sub>50</sub>	6.58	32.84

## 3. Aryl alkynyl ethers

known

according to the  
invention

Synergist ratio	2,3-dihydro-2,2-dimethyl-7-(2-propynyloxy)benzofurane	418
SR <sub>50</sub>	1.8	20.5

Known naphthyl alkynyl ether	Synergist ratio SR <sub>50</sub>
1-naphthyl 2-propargyl ether	6.52
1-naphthyl 3-butynyl ether	7.95
2-naphthyl 2-butynyl ether	7.72
2-naphthyl 3-pentynyl ether	9.97

## 4. Alkynyl-oxim-ethers

known

according to the  
invention

Synergist ratio	1-acetonaphthon-oxim (2-propynyl) ether	571
SR <sub>50</sub>	7.79	10.02

Examples for formulation:

Names of the marketed auxiliary materials are given in quotation marks, followed by the makers name.

5

## 1. Preparation of powders

## A)

To 158g of fine-grained perlite 20g of carbofuran and 20g of compound 279, were mixed in a homogenizator to this mixture were added 2g of fatty alcohol polyglycol ether ("G-3920" ICI) and the mixture was homogenized. The powder mixture was grained in an ejector mill and to it were added 5g of octyl-phenol-polyglycol-ether (EO=20) ("Triton X-165" Rohm & Haas) and 2g of alkyl-sulfosuccinate ("Aerosol-13" Cyanamid). The resulting product is a wettable powder mixture (WP).

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## B)

10g of compound 279 and 10g of carbofuran were diluted with 2g of ethanol. The solution was mixed in a powder homogenisator with 5g of calcium-lignin-sulfonate ("Borrespeseca" Borregard), 5g of nonyl-phenol-polyglycol-ether (EO=20) ("Arkopal N-200" Hoechst), and 70g of calcium carbonate. The resulting product was grained in an alpine-100 typ mill. Average particle size was 1-2  $\mu\text{m}$ . This composition may be used to prepare microsupensions.

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## C)

The mixture of 3g of Diazinon, 3g of compound 441, and 0.3g of fatty alcohol-polyglycol-ether ("G-3920" ICI) was taken up in a homogenisator apparatus on the mixture of 1.0g synthetic silicic acid (Aerosil 200) and 191g talc ( $d_{\text{max.}}=15-30 \mu\text{m}$ ), the pH of the latter was previously adjusted to pH=7.0 with potassium-

30

and sodium-phosphate buffer. Under further stirring 1g of dioctyl-sulfosuccinate ("Aerosol OTB" Cyanamid) and 1g of fatty alcohol-polyglycol-ether-sulfonate ("Genapol LRD" Hoechst) were added and finally the mixture was grained to an average particle size of 20  $\mu\text{m}$ . The resulting product is an easy  
5 flowing powder preparation.

## 2. Preparation of emulsion concentrates

### 10 A)

The mixture of 5g of pirimicarb and 5g of compound 493 was dissolved in the mixture of 20g of xylene and 40g of propanol. To this solution was added the mixture of 4g of ethoxylated alkyl-phenol + lineare alkyl-aryl-sulfonate-calcium salt ("Geronol FF/U Geronazzo) and 6g of ethoxylated amine + fatty acid +  
15 lineare alkyl-aryl-sulfonate alkali metal salt ("Geronol MS" Geronazzo). After complete dissolution 20g of water were added. Transparent solution was obtained, for which is characteristic, that on dilution with water it forms an emulsion of 0.8-1.5  $\mu\text{m}$  drop-diameter.

### 20 B)

The mixture of 5g of quinalphos and 10g of compound 484 and the mixture of 7g of ethoxylated-(EO=13)-propoxylated-(PO=21)-nonylphenol, 2g of lineare-dodecylbenzenesulfonic acid-calcium salt and 12g POE-(20)-sorbitan-monooleate were dissolved in the mixture of 28.6-28.6 ml of propyleneglycol  
25 and pine-fatty acid and 23.8ml of sun-flower oil, 9.5ml of etanol and 95 ml of aliphatic hydrocarbone with 45% naphthene content. The material thus obtained may be preferably used for the preparation of microemulsions.

### C)

30 The mixture of 0.02-0.02 parts by mass of the active ingredient and of the synergist is dissolved in 10 parts by mass of propanol, to the resulting solution

99.96 parts by mass of odourless petroleum are added and the mixture is stirred until a homogenous solution is obtained. The resulting oily dispersible preparation can directly be used in ULV applications.

5 D)

The method described in example A) is followed, with the difference that 10g of compound 279 is applied as synergist active ingredient.

10 3. Preparation of granulates

In a mechanical granulator are mixed 300g of carbofuran, 300g of compound 418, 1500g of polycarboxylate alkali salt ("Sorphol." Toho), 500g of dodecyl-benzenesulfonic acid sodium salt ("Marlon TP 370" Hüls), 500g of beet sugar and 7200g of caolinite. The powder mixture thus obtained is mixed with 8300ml  
15 of water using a mixer of high shear force ( $v=10\text{m/s}$ ). The mixture is finally spray-dried. Particle-size distribution of the product is 0.1-0.4 mm.

4. Preparation of aerosols

20

In a 100 l apparatus supplied with stirrer are mixed 1kg of bioallethrin, 0.5kg of compound 441, 0.1kg of aerosil-air 972, 0.1 kg of ethyleneglycol-monosalicylate, 15kg of odourless petroleum and 50kg of propanol. After dissolution it is filled into cylinders with 33.3kg of liquid propane-butane  
25 (25-75) gas.

### 5. Preparation of vaporators

In 60 ml of ethanol are dissolved 5g of S-bioallethrin, 5g of compound 279 and 1 g of lemon aroma. The solution is applied in vaporators, at a temperature of 50 °C.

**What we claim is:**

- 1.) Compounds of the general formula I . their optically active isomers and salts  
- wherein
- 5 Ar = alycyclic, aromatic or one or more heteroatom containing heterocyclic moiety, optionally substituted by one or more alkoxy-, methylenedioxy-, alkyl-, halogen-, haloalkyl-, or nitro-group and/or condensed with a benzene ring;  
R<sup>1</sup>, R<sup>2</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl,
- 10 R<sup>3</sup>, R<sup>4</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, or  
R<sup>3</sup>, R<sup>4</sup> are together =O,  
Y= C; PO, or
- 15 YR<sup>3</sup>R<sup>4</sup> together  $\begin{array}{c} \text{R}^9 \\ | \\ -\text{C}=\text{N}- \end{array}$  group;  
X = -O-; -NR<sup>10</sup>;  
R<sup>9</sup> = H, alkyl, phenyl, substituted phenyl;  
R<sup>10</sup> = H, alkyl;
- 20 R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> are independently H, alkyl, alkenyl, haloalkyl, or  
Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(YR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X- form together a carboximide group;  
E = H, halogen, methyl;  
m = 0, 1, 2 ;  
n = 0, 1 ;  
o = 0, 1, 2 ;
- 25 p = 0, 1, 2,  
with the proviso, that the sum of the atoms or groups of the -(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X-(CR<sup>5</sup>R<sup>6</sup>)<sub>o</sub>-(CR<sup>7</sup>R<sup>8</sup>)<sub>p</sub> bridge sceleton is 3 and the -C≡C-E sceleton forms with the atoms of the bridge a linear chain, consisting of 6 atoms ending preferably in a methyl group,



furthermore with the proviso, that if Ar stands for a naphthyl group. Y means C-atom. X means O-atom. R<sup>3</sup> and R<sup>4</sup> together can not mean =O.

- 2.) Compounds of general formula IA and their optically active isomers - where  
5 Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o and p have the same meanings as defined in claim 1.
- 3.) Compounds of general formula IB and their optically active isomers - where  
10 Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, Y, E, m, o and p have the same meanings as defined in claim 1.
- 4.) Compounds of general formula IC and their optically active isomers - where  
Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o and p have the same meanings  
15 as defined in claim 1.
- 5.) Compounds of general formula ID and their salts and optically active  
isomers - where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, E, m, n, o and p  
have the same meanings as defined in claim 1.
- 20 6.) Compounds of general formula IE and their salts and optically active isomers  
- where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, E, m, n, o and p have the  
same meanings as defined in claim 1.
- 7.) Compounds of general formula IF and their optically active isomers - where  
25 Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, o and p have the same meanings as  
defined in claim 1.
- 8.) Compounds according to claim 1.  
1-naphthylmethyl 2-butyryl ether,  
30 2-propynyl-1,3-benzodioxol-5-carboxylate,  
- 1-[(2-butyryloxy)-ethyl]-3,4-dimethoxybenzene.

2,6-dichloro-1-(2-butynyloxy-methyl)benzene,

1-[1-(2-butynyloxy) propyl]naphthalene,

R-(+)-2-[1-(2-butynyloxy) ethyl]naphthalene.

5-[(but-2-ynyloxy)methyl]-1,3-benzodioxole.

5 5-[2-methyl-1-(2-butynyloxy)propyl]-1,3-benzodioxole.

5-[(but-2-ynyloxy)phenylmethyl]-1,3-benzodioxole

2-[(2-butynyloxy) methyl]-1,4-benzodioxane,

2,3-dihydro-2,2-dimethyl-7-(3-pentyloxy)benzofurane.

10 9.) Process for the preparation of compounds of general formula I. where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, X, Y, E, m, n, o, and p, have the same meanings as defined in claim 1.

characterized by, that

15 a.) for the preparation of compounds of general formula IA, where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meanings as defined in claim 1.,

compounds of general formula II and III are reacted. where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meanings as defined in claim 1.,

20 A and B are groups suitable to form ester bond,

b.) to prepare compounds of general formula IB, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, Y, E, m, o, and p, have the same meanings as defined in claim 1.,

compounds of general formula IV and V are reacted. where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>,

25 R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, Y, E, m, o, and p, have the same meanings as defined in claim 1., and C and D are groups suitable to form amide bond.

c.) to prepare compounds of general formula IC, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meanings as defined in claim 1., R<sup>3</sup>

30 and R<sup>4</sup> independently mean H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl,

compounds of general formula VI and VII are reacted. wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p have the same meanings as defined in claim 1.. R<sup>3</sup> and R<sup>4</sup> independently mean H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl. F and G are groups suitable to form ether bond.

5

d.) to prepare compounds of general formula ID, wherein Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>2</sup>R<sup>4</sup>)<sub>n</sub>-N- stands for a carboximide group. R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, o, and p, have the same meanings as defined in claim 1..

the carboximide of general formula VIII is reacted with the compound of  
10 general formula IX, wherein R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, o, and p, have the same meanings as defined in claim 1. and Lg represents a leaving group,

e.) to prepare compounds of general formula IE, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>10</sup>, E, m, n, o, and p, have the same meanings as defined in  
15 claim 1..

compounds of general formula X and XI are reacted. wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, E, m, n, o, and p, have the same meanings as defined in claim 1., H and I represent groups, suitable to form a  
-N-

20 R<sup>10</sup>

group where the meaning of R<sup>10</sup> is the same as defined in claim 1..

f.) to prepare compounds of general formula IF, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, o, and p, have the same meanings as defined in claim 1..

25 compounds of general formula XII and IX are reacted. where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, E, m, n, o, and p, have the same meanings as defined in claim 1.. and Lg represents a leaving group, and

if desired, the compound of general formula I thus obtained is transformed into  
30 its salts, or liberated from its salts, and, if desired, the optically active isomers are separated.

10.) Pesticide composition comprising as active ingredient 0.0001-99.9 % by mass of a compound of the general formula I.

where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, m, n, o and p have the  
5 same meanings as defined in claim 1.,  
and optionally other pesticide active ingredient(s), beside carriers and other auxiliary materials.

11.) Arthropodicide composition comprising as active ingredient 0.0001-99.9 % by mass of a compound of the general formula I.

where Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, m, n, o and p have the  
same meanings as defined in claim 1.,  
and optionally other arthropodicide active ingredient(s), beside carriers and other auxiliary materials.

15

12.) Composition according to claim 11, characterized by, that it contains as other active ingredient

Acetamide derivatives: e.g. oxamyl;

20 Benzoylurea compounds: e.g. flucycloxuron, hexaflumuron, teflubenzuron, triflumuron;

Benzoylurea like IGR compounds;

Bicycloheptadien compounds: e.g. heptenophos;

Cross-bridged diphenyl compounds: e.g. etofenprox, bromopropylate, methoxychlor, temephos, tetradifon;

25 Carbamates: e.g. aminocarb, aldicarb, aldoxycarb, asulam, bendiocarb, benfuracarb, carbaryl, carbetamide, carbofuran, carbosulfan, diethofencarb, dioxacarb, ethiofencarb, fenobucarb, fenoxycarb, furathiocarb, isoprocarb, methomyl, oxamyl, pirimicarb (pirimor), propoxur, thiodicarb, thiofanox, xylylcarb;

30 Carbamoyloxime derivatives: e.g. alanycarb, butocarboxim;

Cyclodienes: e.g. aldrin, chlordane, endosulfan, heptachlor;

- Diazoles: fipronil;  
Hydrazides: RH 5992, RH 5849, CGA 215'944;  
Nereistoxin analogues: pl. bensultap;  
Nitroimidazolidynlenamines: e.g. imidacloprid;
- 5 Organophosphor compounds e.g. quinalphos, diazinon, phosalone, dimethoate, azinphos-methyl,  
Organotin compounds e.g. azocyclotin, cyhexatin, fenbutatin oxide SSI-121;  
Phenoxy compounds: e.g. diafenthiuron;  
Pyrazoles: e.g. pyrazophos;
- 10 Pyrethroides: e.g. allethrin, bioallethrin (esbol), acrinathrin, fenvalerate, empenethrin, prallethrin, resmethrin, MTI-800, flufenprox, permethrin, tetramethrin, cypermethrin and their isomers and isomer-combinations;  
Pyridazinones: e.g. pyridaben;  
Pyridine derivatives: e.g. chlorpyrifos;
- 15 Pyrimidine derivatives: e.g. pyrimiphos-ethyl, pyrimiphos-methyl;  
Pyrroles: e.g. AC 303-t, 630;  
Quinazolines: e.g. fenazaquin;  
Terpenoid derivatives: e.g. methoprene;  
Tetrazines: e.g. clofentezine, SzI-121 (flufenzin);
- 20 Thiadiazines: e.g. buprofezin;  
Thiazolidin: pl. hexythiazox;  
Triazoles: pl. isazophos, RH 7988;  
Chlorinated hydrocarbons: lindane;  
Macrocyclic lactones;
- 25 Tebufenpyrad;  
Fenpyroximate;  
Triazamate;
- 13.) Compositions according to claims 11. and 12, comprising a s active  
30 ingredient of general formula I one or more of the following compounds:  
1-naphthylmethyl 2-butyryl ether,

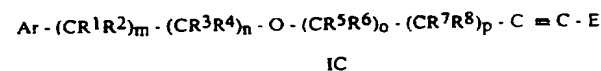
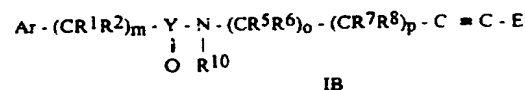
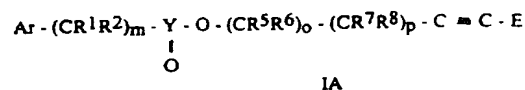
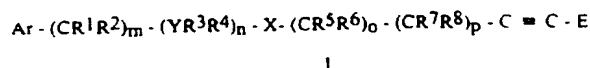
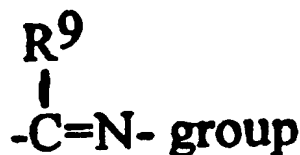
- 2-propynyl-1,3-benzodioxol-5-carboxylate.  
1-[(2-butynyloxy)-ethyl]-3,4-dimethoxybenzene.  
2,6-dichloro-1-(2-butynyloxy-methyl)benzene.  
1-[1-(2-butynyloxy)propyl]naphthalene,  
5 R-(+)-2-[1-(2-butynyloxy)ethyl]naphthalene,  
5-[(but-2-ynyloxy)methyl]-1,3-benzodioxole,  
5-[2-methyl-1-(2-butynyloxy)propyl]-1,3-benzodioxole.  
5-[(but-2-ynyloxy)phenylmethyl]-1,3-benzodioxole.  
2-[(2-butynyloxy)methyl]-1,4-benzodioxane,  
10 2,3-dihydro-2,2-dimethyl-7-(3-pentyloxy)benzofuran.
- 14.) Composition according to claims 11-14 comprising as active ingredient  
0.0001-99.9 % by mass of a compound of the general formula I, where Ar, R<sup>1</sup>,  
R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, m, n, o and p have the same meanings as  
15 defined in claim 1., and a carbamate suitable for extermination of arthropoda,  
preferably carbofuran.
- 15.) Composition according to claim 14 containing (2-butynyloxy-methyl)-3,4-  
dimethoxybenzene, as compound of the general formula I.  
20
- 16.) Composition according to claim 14 containing 5-[(but-2-ynyloxy)methyl]-  
1,3-benzodioxole, as compound of the general formula I.
- 17.) Process for extermination of pests, preferably arthropoda, comprising  
25 treating pests, preferably arthropoda with a suitable amount of a composition of  
claims 10 or 11, if desired in such a way that the compositions containing  
compounds of the general formula I, wherein Ar, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>,  
R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, m, n, o and p have the same meanings as defined in claim 1., and  
the compositions containing the known active ingredients are used in a tank  
30 mixture or subsequently.



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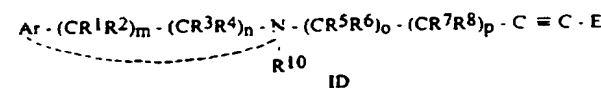
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(54) Title: PESTICIDE COMPOUNDS, COMPOSITIONS AND PROCESS FOR THE PREPARATION THEREOF



## (57) Abstract

The invention relates to compounds of general formula (1), their optically active isomers and salts wherein Ar = alicyclic, aromatic or one or more heteroatom containing heterocyclic moiety, optionally substituted by one or more alkoxy-, methylenedioxy-, alkyl-, halogen-, haloalkyl-, or nitro-group and/or condensed with a benzene ring; R<sup>1</sup>, R<sup>2</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, R<sup>3</sup>, R<sup>4</sup> = independently H, alkyl, alkenyl, haloalkyl, phenyl, substituted phenyl, cycloalkyl, or R<sup>3</sup>, R<sup>4</sup> are together -O, Y = C, PO, or YR<sup>3</sup>R<sup>4</sup> together (a) group; X = -O-, -NR<sup>10</sup>-, R<sup>9</sup> = H, alkyl, phenyl, substituted phenyl; R<sup>10</sup> = H, alkyl; R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> are independently H, alkyl, alkenyl, haloalkyl, or Ar-(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(YR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X- form together a carboximide group; E = H, halogen, methyl; m = 0, 1, 2; n = 0, 1; o = 0, 1, 2; p = 0, 1, 2, with the proviso, that the sum of the atoms or groups of the -(CR<sup>1</sup>R<sup>2</sup>)<sub>m</sub>-(CR<sup>3</sup>R<sup>4</sup>)<sub>n</sub>-X-(CR<sup>5</sup>R<sup>6</sup>)<sub>o</sub>-(CR<sup>7</sup>R<sup>8</sup>)<sub>p</sub> bridge skeleton is 3 and the -C≡C-E skeleton forms with the atoms of the bridge a linear chain, consisting of 6 atoms ending preferably in a methyl group, furthermore with the proviso, that if Ar stands for a naphthyl group, Y means C-atom, X means O-atom, R<sup>3</sup> and R<sup>4</sup> together cannot mean -O. The compounds of general formula (1) according to the invention can be applied as active ingredients of pesticide, preferably arthropodicide compositions, and as synergists of other arthropodicide active ingredients.



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CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam



# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/HU 96/00069

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C43/166 A01N31/04 C07C43/215 C07C43/176 C07D317/48  
C07D307/79 C07D319/20 A01N31/16 A01N43/30 A01N43/32  
A01N43/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, vol. 16, no. 5, 1968, WASHINGTON US, pages 779-786, XP002029949 R. M. SACHER ET AL: "Propynyl naphthyl ethers as selective carbamate synergists" cited in the application see Table I, compound no. XIII and Fig. 1 ---	1,4, 9-12,17
X	US 3 954 793 A (D. J. HENNESSY) 4 May 1976  see column 2, line 32 - column 4, line 55; examples 1,2,5,6 & DE 22 35 005 A cited in the application ---	1,4,7, 9-12,14, 17
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

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- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- \*&\* document member of the same patent family

Date of the actual completion of the international search

28 April 1997

Date of mailing of the international search report

26.05.97

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# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/HU 96/00069

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	US 3 718 686 A (M. S. CHODNEKAR) 27 February 1973 see column 4, line 3 - column 7, line 24; examples 44-48 ---	1,2,4, 9-11,17
X	US 3 402 179 A (K. F. MINOO-SHI) 17 September 1968 see example 1; table 1 & NL 6 600 916 A cited in the application ---	1,5, 9-12,17
A	GB 2 161 163 A (KUREHA KAGAKU KOGYO) 8 January 1986 see claims -----	1,2, 9-11,17

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